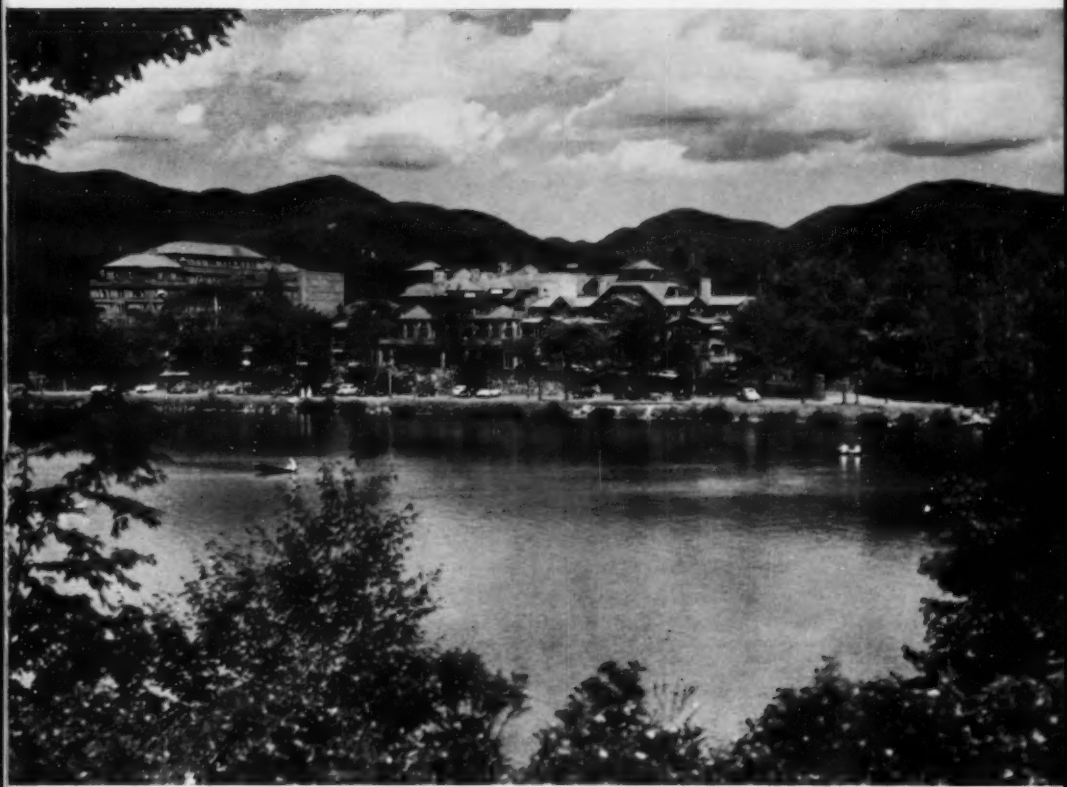
THE JOURNAL
OF THE
AMERICAN LEATHER CHEMISTS ASSOCIATION

VOL. LII MARCH 1957 No. 3



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The Journal

of the

AMERICAN LEATHER CHEMISTS ASSOCIATION

Vol. LII MARCH 1957 No. 3

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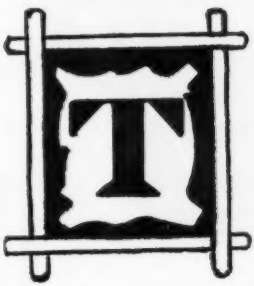

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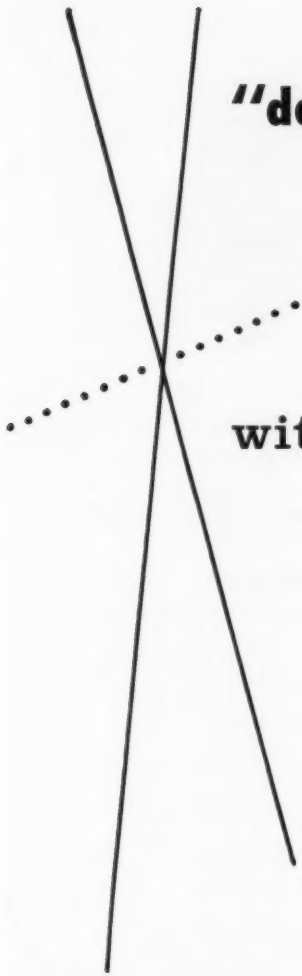

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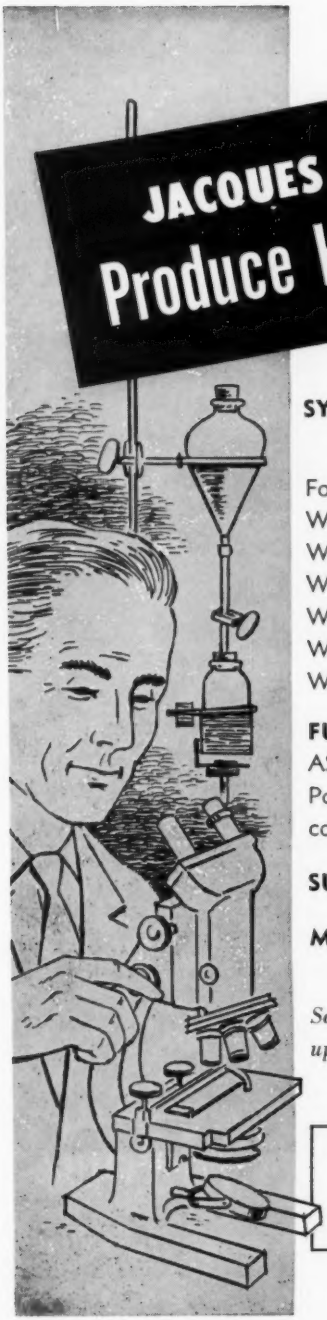

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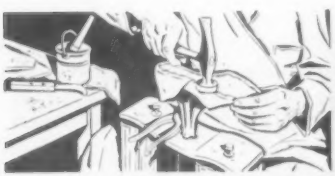

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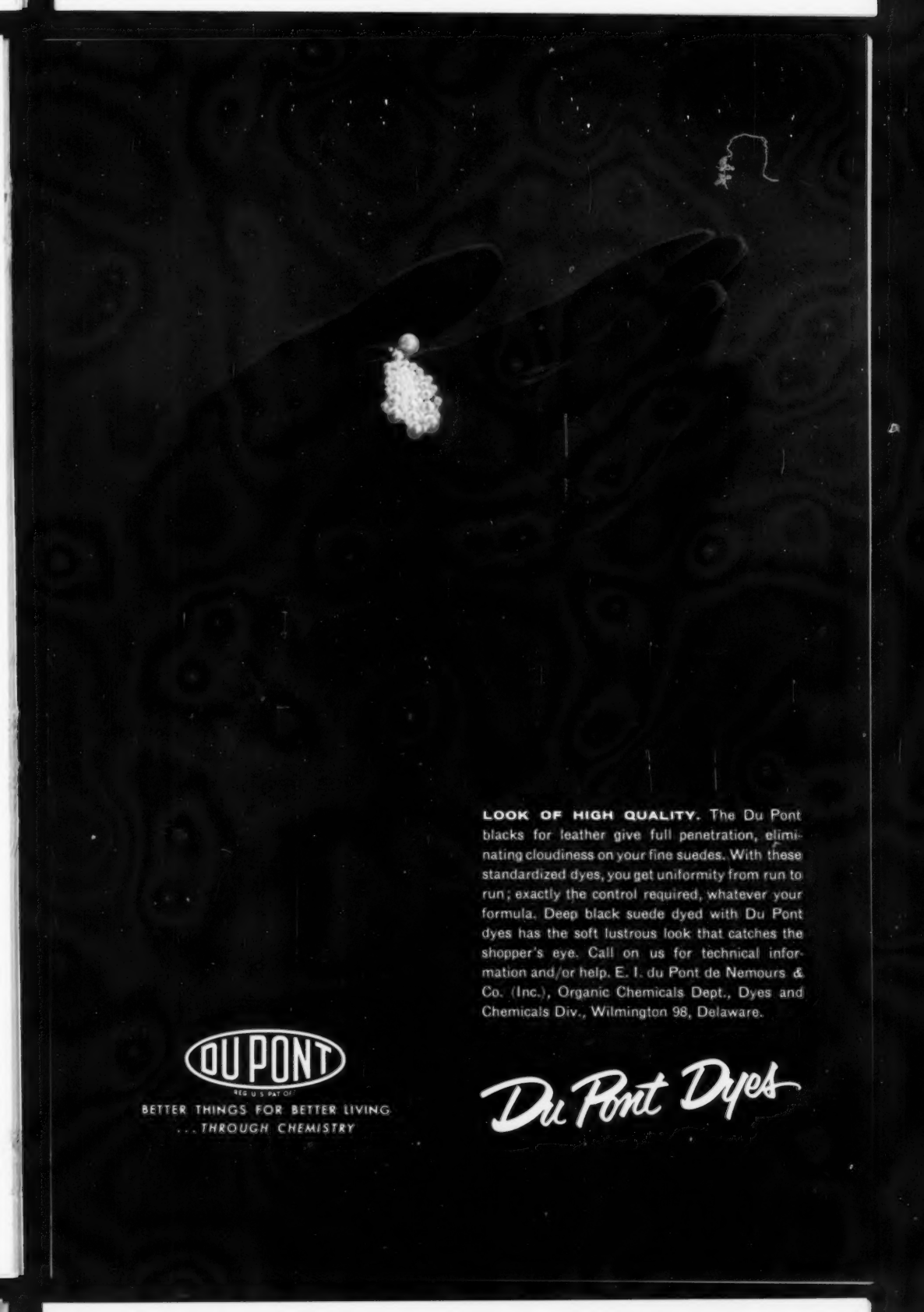

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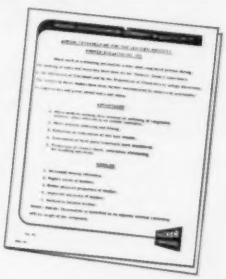

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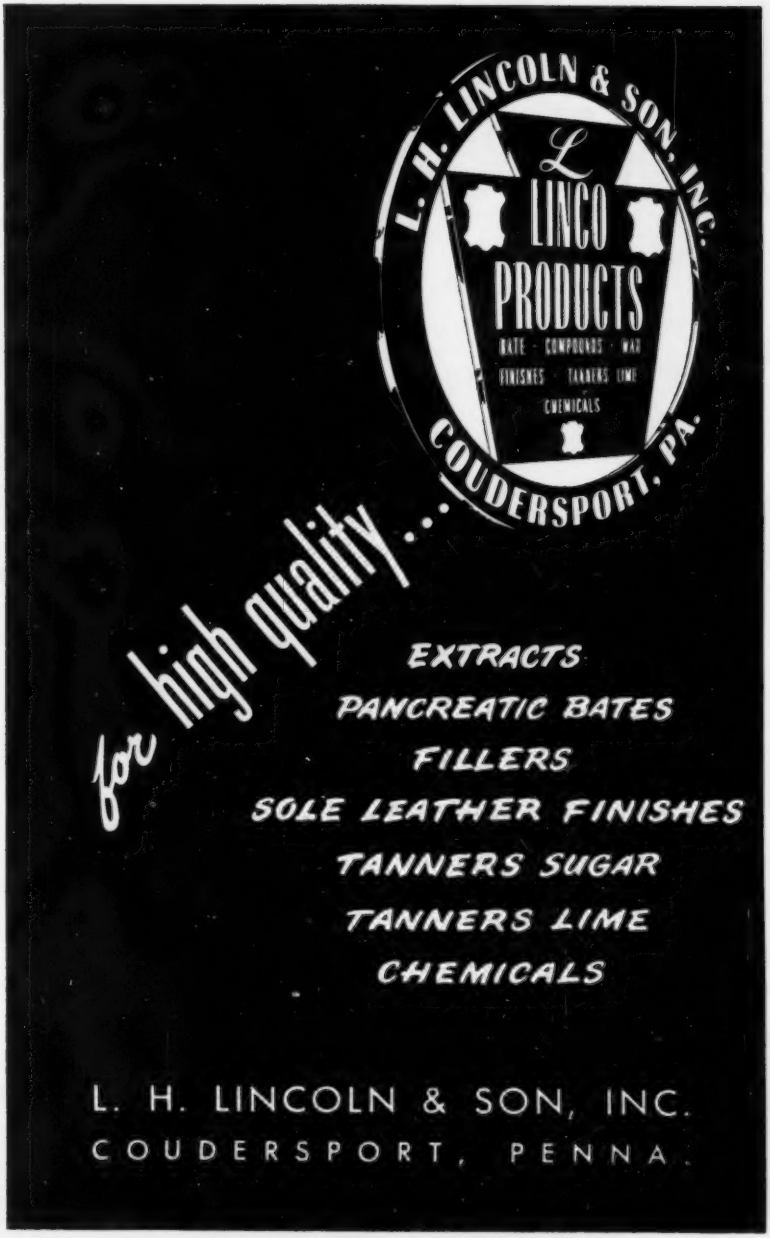
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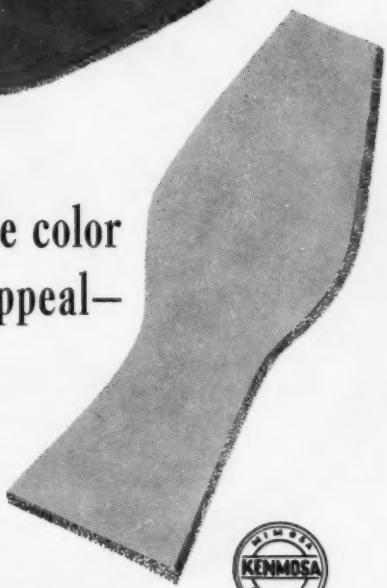

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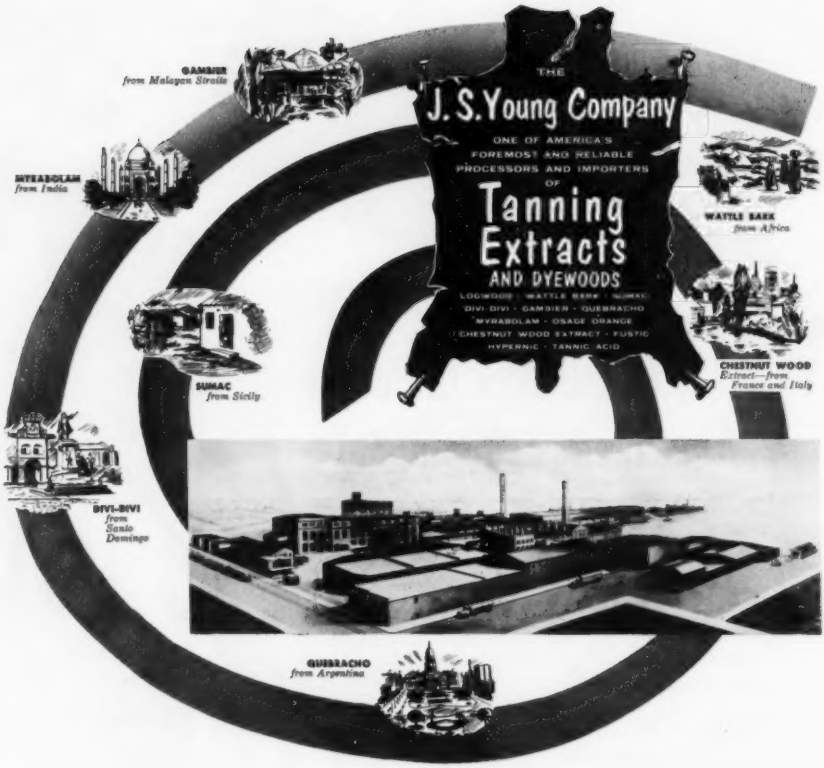

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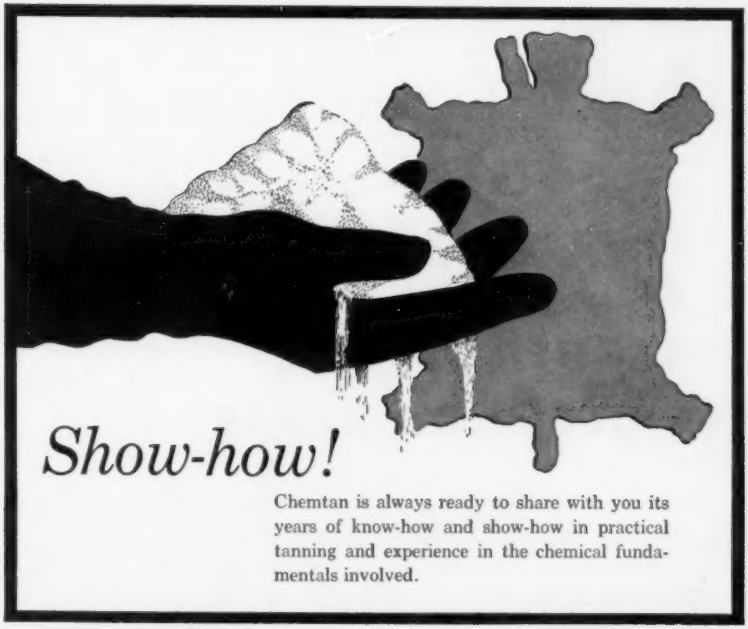

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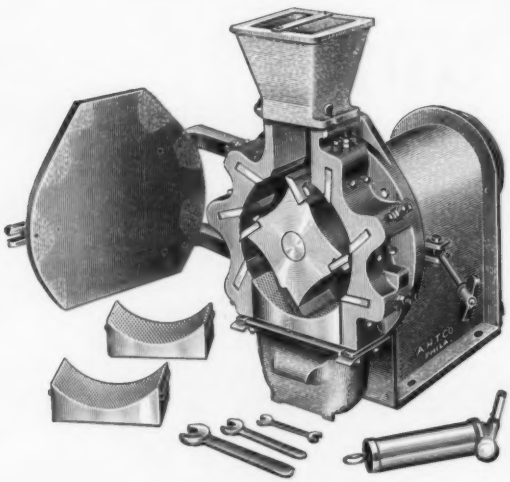

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PHYSICAL PROPERTIES OF LEATHER FATLIQUORED AT DIFFERENT OIL LEVELS*

VICTOR MATTEI AND WILLIAM T. RODDY

Tanners' Council Research Laboratory
University of Cincinnati
Cincinnati 21, Ohio

ABSTRACT

The physical properties of chrome-tanned leather fatliquored at different oil levels give information that is important in elucidating the fatliquoring mechanism. In the present study the amount of oil taken up by the leather was varied by fatliquoring at different oil oil levels. The tests used to measure the physical properties were tongue tear, stitch tear, tensile strength, elongation component, needle puncture and hardness. Statistical analyses of the data were made, and the data are presented to show the influence of the amount of oil on the physical properties of the leather. Cross-sections of the leather were prepared and studied to determine the deposition at the different oil levels.

INTRODUCTION

The influence of oil on the physical properties of leather is important for an understanding of the mechanism of fatliquoring. However, such an elucidation of the mechanism of fatliquoring is dependent upon the physical measurements of leather. For example, the stress-strain measurements of leather below the breaking load may be better indicators of how oil influences the physical properties of leather than the stress-strain measurements at the breaking load. The object of this study was to determine what physical test measurements best indicate the influence of oil on the physical properties of leather. It seemed logical to begin the study by comparing physical properties of fatliquored leather with those of nonfatliquored leather in order to determine what tests best distinguish the fatliquored leathers, and then to continue the study by comparing the physical properties of leather fatliquored at different oil levels. The physical properties of fatliquored leather compared to solvent-extracted leather which best distinguished the influence of the fatliquor were given in a previous article (2). That paper

*Presented at Fifty-second Annual Meeting, Mackinac Island, Michigan, June 19, 1956.

made reference to past studies and also indicated the need of statistically designed experiments for a study of this kind.

On the basis of this information the study of the physical properties of fatliquored stock was extended. In the present study the amount of oil taken up by the leather was varied by fatliquoring at different oil levels.

Since the type of leather and oil used might influence the results obtained, all the tests were made on chrome-tanned kip skins, and a mixture of sulfated cod oil–raw cod oil was used for fatliquoring. The standard of comparison between treatments within an experiment was leather fatliquored to a 6% oil level. The fatliquored samples were not staked.

The tests used to measure the physical properties were tongue tear, stitch tear, tensile strength, elongation components, needle puncture, and hardness. Statistical analyses of the data were made and are presented in this paper. Cross-sections of the leather were prepared and studied to determine the deposition of the oils.

EXPERIMENTAL

The sampling plan adopted for this experiment contained more samples per treatment than the first study and eliminated the D position (2). In the new sampling plan only positions A, B, and C were used as indicated in Figure 1. Strips from 36 commercially prepared chrome-tanned kip skins in the

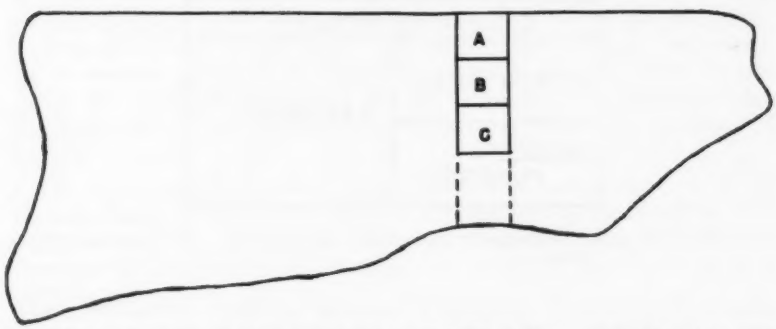


FIGURE 1.—Location of strips, approximately 5″ x 25″, of chrome-tanned kip skins used for tests. The part of each strip below Block C was discarded.

blue were used. A strip was cut from the shoulder of each side as shown in Figure 1. The strips were further subdivided into 5″ x 5″ blocks. After the 108 blocks had been cut and marked, they were divided into four groups as directed by a random distribution table. Each group contained a total of 27 blocks per treatment. The random distribution of the specimens minimized the between-skin variation, leaving only two variables to account for in the analysis of variance of the subsequent data, namely, treatment and position.

The treatments consisted of fatliquoring the leather to contain 6, 10, 15, and 18% oil on the moisture-free leather basis. The samples were all fatliquored with a mixture of 60 parts of medium-sulfated cod oil and 40 parts of raw cod oil.

The 5″ x 5″ blocks were milled in twice their weight of water for 15 minutes and then neutralized with a 1% sodium bicarbonate solution on the wet basis of the chromed stock for 30 minutes at 120°F. (2 to 1 float), followed by a milling in the same volume of water for 15 minutes at 120°F. The samples were then fatliquored at 120°F. in twice their weight of liquor to their respective oil levels of 6, 10, 15, and 18%. After fatliquoring, the samples were tacked up to dry at room temperature.

The fatliquored 5″ x 5″ blocks were then cut for testing as shown in Figure 2. The cut specimens were conditioned prior to testing for at least 48

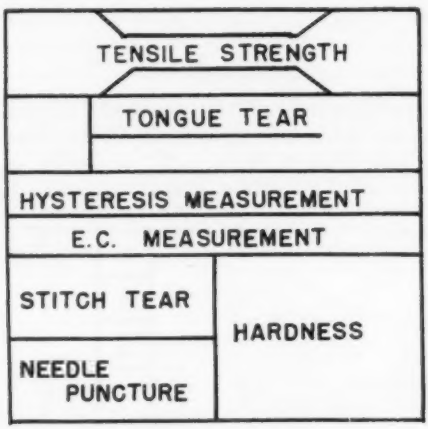


FIGURE 2.—Sampling of blocks for physical test measurements. E. C. means Elongation Component.

hours at 73.4° ± 1.8°F. and 50 ± 4% relative humidity. The following procedures were used in making the physical test measurements:

Hardness—Measured with the Trionic rubber hardness gauge in Shore units.

Needle puncture—Measured on the Schiefer compressometer (3) modified with a needle adapter.

Tensile strength—Dumbbell-shaped specimens 4″ long with ends 1″ x 1″ and centers 0.5″ wide and 2″ long, were measured on the Instron tester at a 500-pound full-scale load, jaw speed of 10″ per minute, chart speed of 20″ per minute, at a jaw span of 2″.

Stitch tear—Standard ALCA specimens were measured on the Instron tester at a 100-pound full-scale load, jaw speed of 10″ per minute, chart speed of 20″ per minute, and a 1.5″ jaw span.

Tongue tear—Specimens 3″ long and 1″ wide with a 2″ slit running through the center of the 1″ width were measured on the Instron tester at a 100-pound full-scale load, jaw speed of 10″ per minute, chart speed of 20″ per minute, and a 2″ jaw span.

Elongation components—5″ x 0.5″ specimens were measured on the Instron tester at a 100-pound full-scale load, 30% extension, jaw speed 5″ per minute, chart speed 20″ per minute, and a 2″ jaw span.

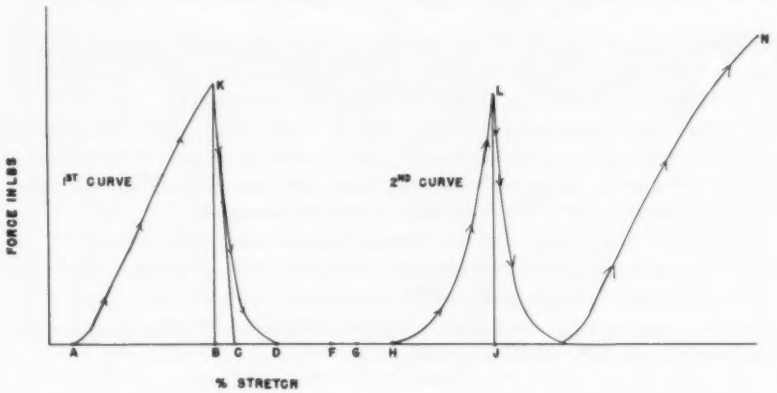
By the above testing procedures 17 physical properties were measured for each leather sample which was fatliquored.*

The Instron Tester utilizes a precision electronic weighing system for detecting and recording the load applied to the specimen under test. The pulling jaw is operated by a unique drive that provides an absolutely controlled rate of elongation of the specimen over a wide range of speeds and in either direction of travel and with instant reversibility. The chart of the high-speed recorder is driven at various speed ratios with respect to the pulling jaw, so that the tensile load–elongation curves of the leather are made accurately, at constant rate of elongation. By proper selection of jaw and chart speed the stress-strain curve obtained can be magnified. By use of readily interchangeable load cells, full-scale sensitivities may be obtained extending from 2 grams up to 1000 pounds or more. The instrument is not limited to measuring stress-strain properties of leather but can be used for such measurements as the stitch-tear and tongue-tear strength of leather. For a more detailed description of the Instron, reference is made to an article by Hindman and Burr (1).

The measurements obtained from the elongation-component curve are given in Figure 3. The force in pounds is represented by the *Y*-axis and the per cent stretch by the *X*-axis. The leather specimens were stretched to a constant 30% extension, and a relaxing period of one minute was allowed between cycles.

The measurements obtained from the elongation-component curves are defined at the bottom of Figure 3. *AB* and *GJ* equal total elongation of 30%, *BC* equals per cent immediate elastic recovery, *HJ* minus *BC* equals per cent delayed recovery, *DF* equals per cent specimen slack, *GH* equals per cent permanent set. *K* and *L* equal force to extend 30% (1st and 2nd cycles), *K* minus *L* equals difference between cycles 1 and 2 in force to extend, *N*

*Figure 2 indicates that test specimens were taken for hysteresis measurements. Both elongation-component curves and hysteresis curves measure stress-strain properties, and the physical test data obtained for the two curves are the same. In this study the two sets of measurements differed with respect to jaw and chart speeds used in running the tests on the Instron. However, comparative data from the two tests showed little difference between the two sets of measurements. It was decided to disregard the data on hysteresis measurements because the elongation-component measurements are easier to read and calculate.



AB & GJ = 30% EXTENSION
BC = IMMEDIATE ELASTIC RECOVERY
HJ-BC = DELAYED RECOVERY
DF = SPECIMEN SLACK
GH = PERMANENT SET
K = FORCE TO EXTEND 30%
L = FORCE TO EXTEND 30%
K-L = DIFF. IN FORCE TO EXTEND AKDA & HLJH
N = TENSILE STRENGTH
AKBA = AREA OF TRIANGLE (WORK TO EXTEND)
BKDB = AREA UNDER CURVE (WORK RECOVERED)
AKBA-BKDB = AREA OF CURVE (WORK LOST)

FIGURE 3.—Type of Elongation Component curves obtained (not drawn exactly to scale).

equals elongation component for tensile strength, *AKBA* equals the area of the triangle (work to extend 30%), *BKDB* equals the area under the curve (work recovered), and *AKBA-BKDB* equals the area of the curve (work lost).

The curve in Figure 3 indicates that it requires a force *K* to increase the length of the leather specimen 30% and that upon releasing the force the sample does not return to its original length. As the force is released the curve *KD* is a straight line for a while and then begins to curve. The linear portion of *KD* means that part of the elongation is recovered immediately as the tension is decreased. The curved portion approaching *D* shows that another part of the elastic recovery takes place after a certain delay. By projecting the linear part of *KD* to the *X*-axis (*KC*), the distance *BC* can be defined as the per cent immediate elastic recovery. The distance *AB* equals the distance *BF*; that is, if the leather specimen had regained all of its extended length a curve *KF* would have been obtained instead of *KD*. Thus the distance *DF* (specimen slack) indicates the per cent increase in length immediately after the force has been totally released. The leather specimen was allowed to rest one minute prior to recycling at *G*. In so doing the distance *DF* decreases, and on recycling the distance *GH*, the per cent of the extended length remaining, is obtained and is denoted as permanent set. Since resting the leather specimen decreases the distance *DF*, then the best estimate of delayed elastic recovery is not *CD* but *HJ* – *BC*, and this distance is denoted as the per cent delayed recovery.

It was the purpose of this study to compare stress-strain properties of leather fatliquored at different oil levels in order to determine if an increase in oil produces significant differences in the stress-strain properties. Since comparison only is desired, any errors involved in obtaining per cent immediate elastic recovery, per cent delayed recovery, and per cent permanent set should not influence the deductions made. The errors referred to are associated with drawing the line *KC* and the rest period of one minute between cycles.

The measurements of hardness, needle puncture, tensile strength, per cent stretch at break, stitch tear, tongue tear, and elongation-component characteristics of the leather specimens are given in bar graph form in Figures 4 and 5. Each value represents the average of 27 specimens tested.

Specimens of the leather samples fatliquored at the various oil levels were cut into cross-sections and stained for fat deposition with Sudan IV and with Nile Blue Sulfate. Variation in oil deposition at the four oil levels was observed in these cross-sections.

RESULTS

To indicate how the raw data were collected and analyzed, an example of the test data for elongation component per cent immediate elastic recovery is given in Table I. The $\bar{X}$ values for columns and rows signify the average values for the four different oil levels and three positions. The data for the other sixteen tests were collected and analyzed in a similar manner.

The physical test data in Figures 4 and 5 show how the four different oil levels influenced the physical properties of leather. These average values for the 17 physical test measurements made are presented in graph form to simplify the presentation of the data. The black bars represent stock fatliquored to a 6% oil level, the striped bars represent stock fatliquored to a 10% level, the speckled bars the stock fatliquored to a 15% level, and the white bars the stock fatliquored to an 18% oil level. The oil-level bars were arranged from left to right to indicate average values from the low oil level to the high oil levels.

The data show differences in average values between the four oil levels for all of the test measurements made. In Figure 4 the measurements for hardness and needle puncture show a stepwise decrease in values as the oil level increases. Tensile strength, elongation component for tensile strength, per cent stretch at break, stitch tear, tongue tear and per cent stretch at tear show a stepwise increase in values as the oil level increases. In Figure 5 the elongation-component measurements for per cent immediate elastic recovery, work lost, work to extend, work recovered, force to extend 30%, and per cent delayed recovery show a stepwise decrease with increase in oil level. The elongation-component measurements for per cent specimen slack and per cent permanent set show a stepwise increase with an increase in oil level. The elongation measurement for difference in force to extend curves 1 and 2 does not show a trend.

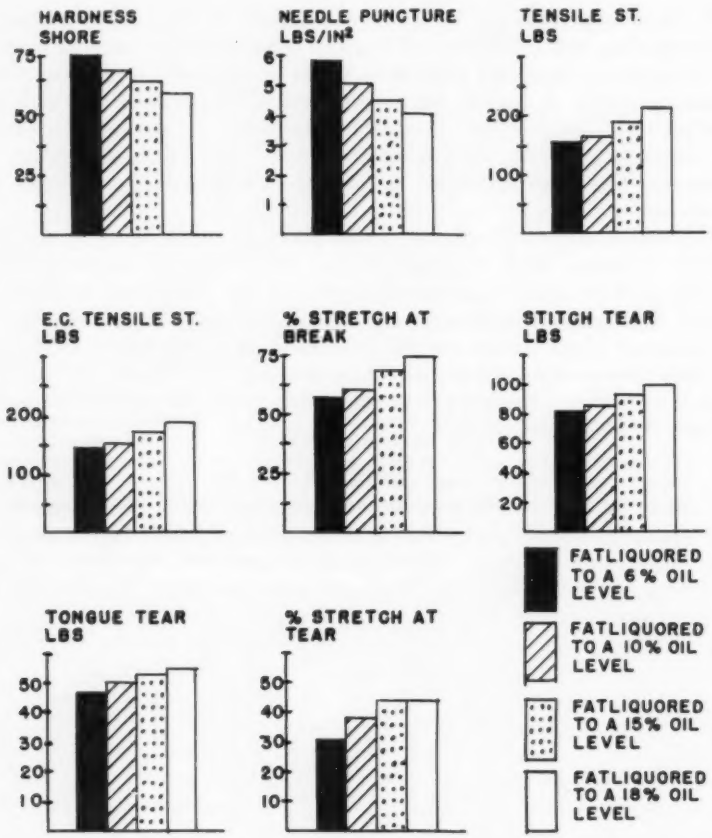


FIGURE 4.—Averages for physical measurements of leathers fatliquored at different oil levels.

The statistical analyses of the above data indicated whether the differences between the averages for different oil levels were large enough to be significant. The analyses further determined whether these averages were being influenced by significant treatment-position interactions and nonhomogenous variances. Thus, the statistics give a better definition of the results.

A two-factor analysis of variance with replications as used in analyzing the raw data is given in Table II. This analysis was obtained from the data on elongation component per cent immediate elastic recovery. Under source of variation are found oil levels, positions, interaction, replication (error term), and total. The rows contain the respective degree of freedom, crude square,

TABLE I

RAW DATA FOR ELONGATION COMPONENT OF PER CENT IMMEDIATE ELASTIC RECOVERY

Position	6% Oil Level	10% Oil Level	15% Oil Level	18% Oil Level	
A	5.38	4.38	4.38	2.88	
A	5.50	4.00	4.50	3.00	
A	5.13	4.38	3.50	2.38	
A	4.88	4.63	4.75	2.88	
A	4.50	4.75	5.13	4.13	4.15
A	4.88	4.13	3.50	3.75	
A	4.38	2.75	3.25	3.75	
A	5.00	5.00	3.75	4.38	
A	5.00	3.75	3.88	3.13	
B	4.13	3.25	2.88	3.88	
B	4.00	4.13	3.50	3.38	
B	4.00	3.75	3.63	3.38	
B	3.88	4.13	3.38	3.75	
B	3.88	2.63	3.13	3.13	3.75
B	4.13	3.13	3.63	3.38	
B	4.25	3.75	4.25	3.75	
B	5.00	3.50	3.00	3.75	
B	5.38	4.25	4.25	3.75	
C	3.88	2.88	2.63	2.88	
C	4.13	3.77	3.00	2.63	
C	4.63	3.75	3.75	3.13	
C	5.25	3.75	3.75	3.25	
C	3.75	3.00	2.50	2.75	3.38
C	3.88	3.13	2.75	2.50	
C	4.75	3.88	3.00	2.75	
C	4.00	2.88	4.00	2.88	
C	3.88	2.75	3.25	2.50	
$\overline{X}$	4.50	3.71	3.59	3.25	

TABLE II

ANALYSIS OF VARIANCE
ELONGATION COMPONENT OF PER CENT IMMEDIATE ELASTIC RECOVERY

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F	Level of Significance
Oil level	3	226477	75492	28.72	High $F > 0.001$ level
Position	2	105257	52628	20.02	High $F > 0.001$ level
Interactions	6	25016	4169	1.59	Not significant
Replication (Error term)	96	252401	2629		
Total	107	609151			

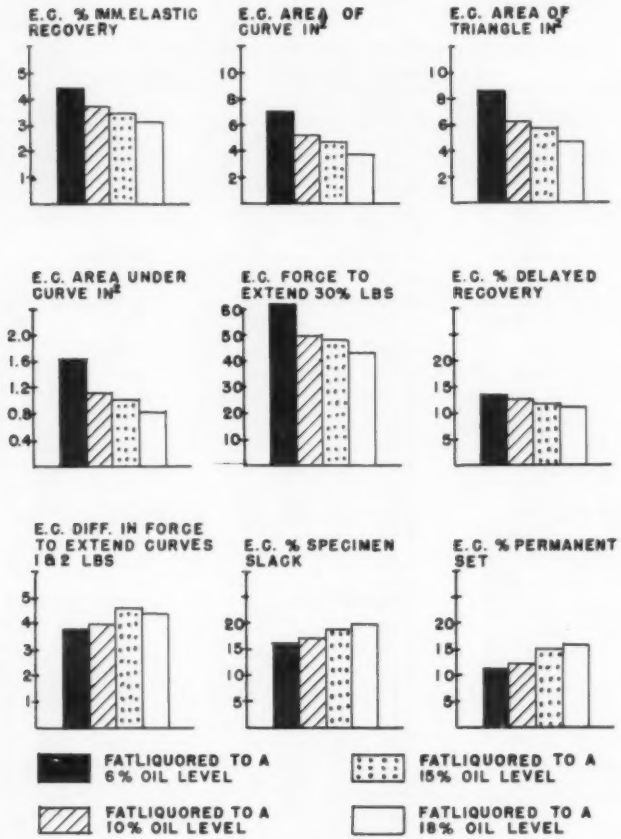

E.C. % IMM. ELASTIC RECOVERY
E.C. AREA OF CURVE IN²
E.C. AREA OF TRIANGLE IN²
E.C. AREA UNDER CURVE IN²
E.C. FORCE TO EXTEND 30% LBS
E.C. % DELAYED RECOVERY
E.C. DIFF. IN FORCE TO EXTEND CURVES 1 & 2 LBS
E.C. % SPECIMEN SLACK
E.C. % PERMANENT SET
FATLIQUORED TO A 6% OIL LEVEL
FATLIQUORED TO A 15% OIL LEVEL
FATLIQUORED TO A 10% OIL LEVEL
FATLIQUORED TO A 18% OIL LEVEL

FIGURE 5.—Averages for physical measurements of leathers fatliquored at different oil levels.

mean square, *F*-values and levels of significance for oil levels, positions, interaction, and replications. The table shows a high level of significant differences between oil-level averages and between position averages.

The analysis of variance for the other sets of data indicated that high levels of significant differences existed between oil-level averages for all the tests except elongation component for difference in force to extend curves 1 and 2, which showed no significant difference. A low level of significant difference between position averages existed for elongation-component force to extend 30%. No significant differences between position averages existed for elonga-

tion-component tensile strength. The other tests showed high levels of significant differences between position averages.

The statistical analysis further indicated that oil-level average and position averages for 7 of the physical test measurements were being influenced by nonhomogeneous variances. The tests so influenced were needle puncture, per cent stretch at break, stitch tear, tongue tear, elongation-component measurements for per cent permanent set, per cent delayed recovery and force to extend 30%. The 10 tests that indicated homogeneous variances were hardness, tensile strength, per cent stretch at tear, elongation-component measurements for tensile strength, work lost, work recovered, work to extend, difference in force to extend curves 1 and 2, per cent immediate elastic recovery, and per cent specimen slack. The position and oil-level averages for the latter tests are significantly different. However, for those tests that indicated high levels of significant differences between oil-level averages, certainly it is safe to assume that significant differences existed between oil-level averages even though nonhomogenous variances were influencing the results.

In agreement with the conclusions arrived at on the basis of the statistical analysis and observation of the raw data, it is observed in Figure 4 that the tensile strength, per cent stretch at break, and elongation-component tensile strength all increase with an increase in oil level. However at a constant 30% extension, the elongation-component measurements of force to extend 30% in Figure 5 decrease with an increase in oil-level average. These data clearly demonstrate the differences in stress-strain properties of leather at and below the breaking force between the 4 different oil levels. This difference is further demonstrated in Figure 5 for elongation-component measurements of per cent specimen slack and per cent permanent set. The increase in these measurements with an increase in oil level indicates that greater fiber slippage and more permanent fiber separation occur as the oil level increases.

In order to complete the study, correlation coefficients were computed to determine if any relationship between test measurements existed. Correlation coefficients were calculated and are presented in Table III. At the top of Table III the different oil levels are given as T_1 (6%), T_2 (10%), T_3 (15%), and T_4 (18%). Each column contains the correlation coefficient for the respective oil levels between the two measurements that were paired.

The asterisks in two rows point out those measurements that had correlation coefficients of 0.85 or better. Such a value is considered indicative of good correlation since the square of 0.85 x 100 indicates that relationships between test values existed 72% of the time.

The values in Table III show that good correlation exists between elongation component for force to extend 30% and its respective work lost and work recovered. Thus, the force at 30% extension is indicative of the work lost and gained and also of the work to extend since the latter value is the sum

TABLE III

CORRELATION COEFFICIENTS (r)

(*E. C.* = *Elongation Component*)

	T_1 (6%)	T_2 (10%)	T_3 (15%)	T_4 (18%)
E. C. force to extend 30% vs. E. C. tensile strength	0.59	0.68	−0.03	0.69
E. C. force to extend 30% vs. E. C. area under curve *	0.95	0.98	0.94	0.95
E. C. force to extend 30% vs. E. C. area of curve *	0.98	0.97	0.98	0.99
E. C. force to extend 30% vs. E. C. difference in force between cycles 1 and 2	0.14	0.41	0.42	0.52
E. C. specimen slack vs. E. C. permanent set	0.82	0.87	0.96	0.61
E. C. specimen slack vs. E. C. immediate elastic recovery	−0.42	−0.61	−0.65	−0.35
E. C. specimen slack vs. E. C. delayed recovery	−0.62	−0.40	−0.73	−0.52
Hardness vs. E. C. specimen slack	−0.48	−0.71	−0.88	−0.74
Hardness vs. E. C. permanent set	−0.57	−0.63	−0.86	−0.62
Hardness vs. E. C. immediate elastic recovery	−0.37	−0.42	−0.59	−0.53
Hardness vs. E. C. delayed recovery	0.23	0.28	0.67	0.33

*See page 119 for explanation of asterisk.

of the other two work values. The correlation coefficients for elongation component for force to extend 30% versus elongation component for tensile strength showed poor correlation even though both measurements were made on the same sample.

The histological study indicated that the deposition of oil in the grain and the flesh side increased with an increase in oil levels, but this was not too noticeable between the 10 and 15% oil levels. There were slight differences in deposition between positions, and the differences became more pronounced as the oil levels increased. The oil did not completely penetrate through the corium even at the 18% oil level. However, in general the depth of oil penetration into the corium increased with an increase in oil level.

CONCLUSIONS

The statistical analyses indicate that for most of the tests high levels of significant differences between oil-level averages and between position averages exist. As indicated in the discussion of the results, the data for 7 of the tests were influenced by nonhomogeneous variances.

The leathers showed a decrease in elongation-component measurement for force to extend 30% with increase in oil level. The average tensile strength, per cent stretch at break, and elongation-component tensile-strength measurements showed the opposite trend. The elongation-component measurements for per cent specimen slack and per cent permanent set increased with an increase in oil level, indicating greater and more permanent fiber slippage. The above information is indicative of how the different oil levels have influenced the stress-strain properties of the leather at and below the breaking strength.

Good correlation was found to exist between elongation-component measurements for force to extend 30% versus work lost and work recovered. Poor correlation was indicated between elongation-component measurement for tensile strength versus force to extend to 30%.

ACKNOWLEDGMENT

The assistance of J. Tancous in running the Instron tests reported in this work is gratefully acknowledged. Thanks are also extended to the Ohio Leather Company for the cooperation given in supplying the shoulder strips and to Nopco Chemical Company for supplying the oils.

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Received November 8, 1956.

DISCUSSION

MR. BERNARD ROLL (Atlas Refinery, Inc.): This report of Mr. Roddy is, in my opinion at least, the most informative work to date relating the physical properties of leather to its oil content. The hysteresis characteristics, and especially the measurement of elongation components under loads considerably below the breaking point, should give us a much better estimate of what to expect in the way of performance of the leather under actual conditions of usage.

We all hope that none of our leather will break when it is being lasted, so properties such as elongation at break and the actual value of tensile strength itself should not be nearly so significant as the stress and strain properties under loads more nearly corresponding to the forces that are being applied during shoe-lasting and similar operations.

Another point of major interest in Mr. Roddy's findings is the fact that he has found an increase in tensile strength with increasing oil levels up through 18%. During the past two years there have appeared two papers, one, I be-

lieve, by Shuttleworth, and one by a group in our Bureau of Standards, reporting that beyond a certain oil level (I think somewhere around 14%) they could expect decreasing tensile strength rather than an increase. I wonder if Mr. Roddy wants to elaborate on that a little bit? More specifically, I wonder if he feels that this business of oil distribution, which he pointed out is all-important, might be the deciding factor here in tensile strength versus oil content.

MR. RODDY: Shuttleworth's work was done on sheep- and goatskin leathers fatliquored to fairly high oil levels, and at that time it was mentioned by Shuttleworth that any increase in strength you might get with fatliquoring oils should be questioned, because there was a possibility that a misinterpretation could be made; that is, if you increased the oil content, you would not necessarily increase the tensile strength. In the work reported by the Bureau of Standards investigators, most of the leather was stuffed leather, in contradistinction to fatliquored leather.

The point I tried to make today, and would like to have clear, is that it is not necessarily the amount of oil you have in the leather, but where it is actually deposited that affects the physical properties. For example, it would be possible perhaps to put a much smaller quantity of oil all the way through the leather and still retain characteristics of leather fatliquored at high oil levels.

MR. W. O. DAWSON (Chemtan Company): I assume from what you have said, Mr. Roddy, that the ratio of sulfated to raw oil was the same in all cases. Did you obtain complete exhaustion of the oil at all the different levels? Also, did you conduct stratographic analyses to determine the distribution of the oil in the different layers, and if not, could you elaborate on your method of estimating the levels of oil deposition?

MR. RODDY: We controlled the ratio of the oil levels by varying the amount of oil in the fatliquor. Good exhaustion was obtained at all levels except for the stock fatliquored to 18% oil. No stratographic analyses were run. However, cross-sections were made and stained both with Sudan 4 for the neutral oil, and Nile Blue Sulfate for the sulfated oil.

I think that you will agree that you will see exactly where the oil is located. When you run a stratograph, you are not necessarily seeing exactly where the oil is. You are merely estimating how much is in a given layer of leather.

MR. DOMINIC MEO, JR. (Salem Oil and Grease Company): Was there any attempt to obtain correlation between the resiliency of the leather and the moisture content of the leather? Have you made any tests varying the percentage of moisture in the leather?

MR. RODDY: We made no such tests. These leathers were conditioned in a standard atmosphere after fatliquoring, but the moisture content was approximately the same at all four oil levels.

Mr. C. E. RETZSCH (Nopco Chemical Company): I would like to ask Mr. Roddy if, in his testing, anything was done with regard to staking of the leather and comparing the results on staked leather with those on unstaked leather, or whether such a test is being planned, since most leathers receive a staking or mechanical work of some kind that affects the oil distribution.

MR. RODDY: I mentioned that the leather was not staked. We eliminated the staking so that we would not have that variable in the test, and specifically for that purpose.

MR. HENRI KRAKOWSKI (Chicago Allis Mfg. Co.): I would like to ask about the hardness test. Is that an accepted method?

MR. RODDY: It is not an accepted method. We reported it last year for measuring the firmness of leather.

MR. KRAKOWSKI: Will you elaborate?

MR. RODDY: The leather is folded back in such a fashion. We put the hardness gauge down on the leather and press it.

MR. KRAKOWSKI: Continuous reading, or do you wait?

MR. RODDY: We take three readings across the specimen.

MR. WILLIAM S. SHORE (Eagle-Ottawa Leather Company): I would like to ask Mr. Roddy if the surface oil does not migrate into the center of the specimen on long storage.

MR. RODDY: You will have to define the storage conditions. But in general there is a possibility of that happening.

An interesting picture of the size and scope of a colonial tannery is contained in Clark's History of Manufacturers in the United States. This tannery in 1653 reported an inventory of 415 hides in bark valued at $2,000, 45 hides in lime worth over $100 and 312 West Indies hides in lime worth over $600, or a total inventory of 772 hides worth $2,700. A century and a quarter later, in 1778, a New Jersey tannery at Trenton had 64 vats, five limes, two water pools, a bark house which would hold 300 cords of wood, a currying shop, a skin dressing shop and facilities for producing leather breeches.

—*Economics of Cattlehide Leather Tanning.* Merrill A. Watson, D.C.S. Chicago: The Rumpf Publishing Company, 1950.

FLEXIBILITY GAUGE

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ABSTRACT

A description is given of a simple, rugged, and portable instrument for measuring the flexibility and resiliency characteristics of both light and heavy leathers. The usefulness of the instrument is illustrated by data obtained on a wide variety of leathers.

INTRODUCTION

Flexibility and temper are important characteristics that determine the usefulness and quality of leather. Yet in everyday practice these properties are seldom measured in terms of numerical values. Most tanners and sorters rely on judgment and experience. Upper leathers are folded, usually along the backbone line, and the hand is run over the fold. This enables an experienced sorter to make a fairly accurate appraisal of quality, based on an over-all composite of flexibility, temper, and feel. Sole leather men evaluate their leather by handling the bend or strip, and judging its springiness and resistance to bending. A test sometimes used for composition soling material is to hold a full-size strip (15″ x 24″) horizontally by one end; if it stands out straight it is considered to have the rigidity desirable in sole leather.

The development of the gauge described in this paper is an attempt to provide a relatively simple method of measuring flexibility. The term "flexibility" is used in preference to "stiffness" because leather is especially valued for its flexibility. To describe the opposite property, the terms "firmness" and "rigidity" have been employed. Actually the gauge measures the force required to flex or bend a specimen under prescribed conditions, so that a high reading indicates low flexibility, and vice versa. The gauge also permits the measurement of residual firmness after the specimen has been flexed repeatedly. The degree to which resistance to flexure is retained is related to resiliency, which is one factor in "temper".

The gauge was developed from an earlier device used in the dynamic testing of waterproofness of light leathers, where flexibility is a factor in the rate of water penetration. As it was felt that the method might have general usefulness for testing leather, an improved, compact form of the apparatus was

*Presented at the Fifty-second Annual Meeting of the American Leather Chemists Association, Mackinac Island, Mich., June 17 – 20, 1956.

developed, and an attachment for testing heavy leathers was added. Because the force required to flex or bend the specimens is relatively high, it is possible to obtain accurate results while employing a less precise construction than is generally required in instruments for testing stiffness. The gauge is rugged and portable, and thus well suited to plant or on-the-spot testing.

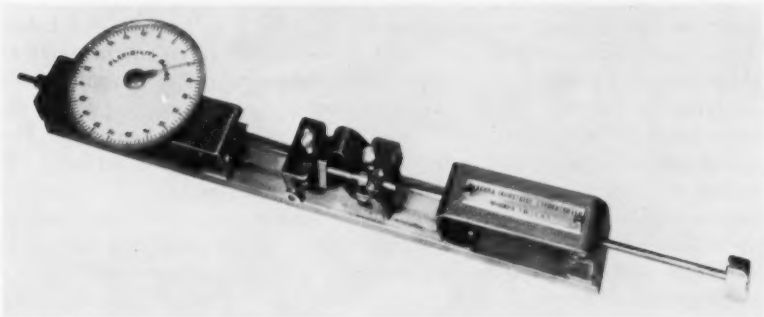

FIGURE 1.—Flexibility gauge as used for cup fold test.

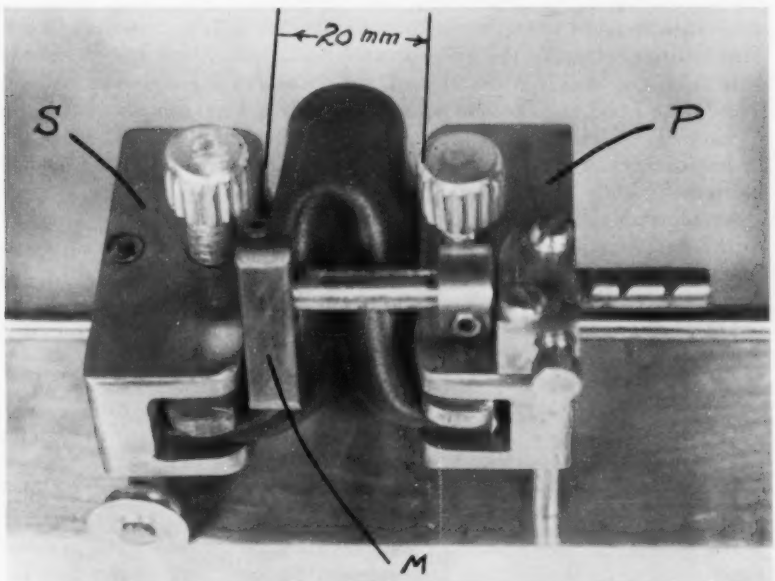

FIGURE 2.—Details of clamps and fully cupped specimen: *P*, push clamp; *S*, scale clamp; *M*, adjustable swivel stop.

APPARATUS

A general view of the gauge, as used for testing light leathers, is given in Figure 1, and for heavy leathers in Figure 7. The gauge consists essentially of two rods, supported in line with each other by brackets attached to a base, which permit free movement of the rods together and apart. Clamps (*S*, *P*, Figure 2) 1¾″ wide, are mounted on the adjacent ends of the rods. These hold the light leather specimens for the cupping test, as described below. Attachments for making the bending test on heavy leathers are mounted on these clamps (Figure 7). At the outer end of the push rod is a hand knob for applying the force to "cup" or bend the specimen. The opposite end of the other rod is tied to a spring which measures the amount of force applied. This spring connects with a dial scale. The spring has a zero point setting. The spring and dial are selected and calibrated to read in ounces. The scale is easy to read, and as the pointer can turn through several revolutions, readings up to about 400 ounces can be obtained. Thus a wide range of loads can be measured, and leathers that vary widely in flexibility can be tested using a single gauge. However, for extremely flexible leathers, a lighter spring and a gauge reading from 0.1 to 10 ounces would be necessary. Suitable straight push-type spring scales are commercially available. There are two legs under the push clamp, *P*, which prevent it from turning, and two small, low-friction wheels are attached to the bottom of the scale clamp, *S*, to center it and prevent twisting. Usually the gauge is used horizontally, with the end of the base against a block. When so used, the friction of the scale and rod was found to be 3 ounces. The zero point of the scale is set to compensate for this friction. The friction can be reduced by mounting the instrument vertically (a less convenient arrangement) or by supporting the scale clamp on ball bearings.

An adjustable distance marker and swivel stop (*M*, Figure 2) is attached to the push clamp. When repeated flexings are to be made this swivel is turned down so that it strikes the opposing clamp, *S*, and thus limits the flex distance to the prescribed amount.

The base of the gauge measures 1½″ x1 6″, and the whole unit weighs 3 pounds.

TESTING LIGHT LEATHERS (CUPPING TEST)

As the methods for testing light and heavy leathers differ, the procedures and results for each type are given separately.

The standard light leather specimen is a piece 2 7/8″ square which is folded evenly on itself, grain out. The ends of the doubled-over piece are inserted in the clamps, previously set 50 mm. apart by means of a collar and set-screw on *P* (Figure 1), which stops against the push rod support bracket when the rod is pulled out as far as it will go. The specimen is held securely in the clamps by tightening the knurled screws on *S* and *P* (Figure 2). In all

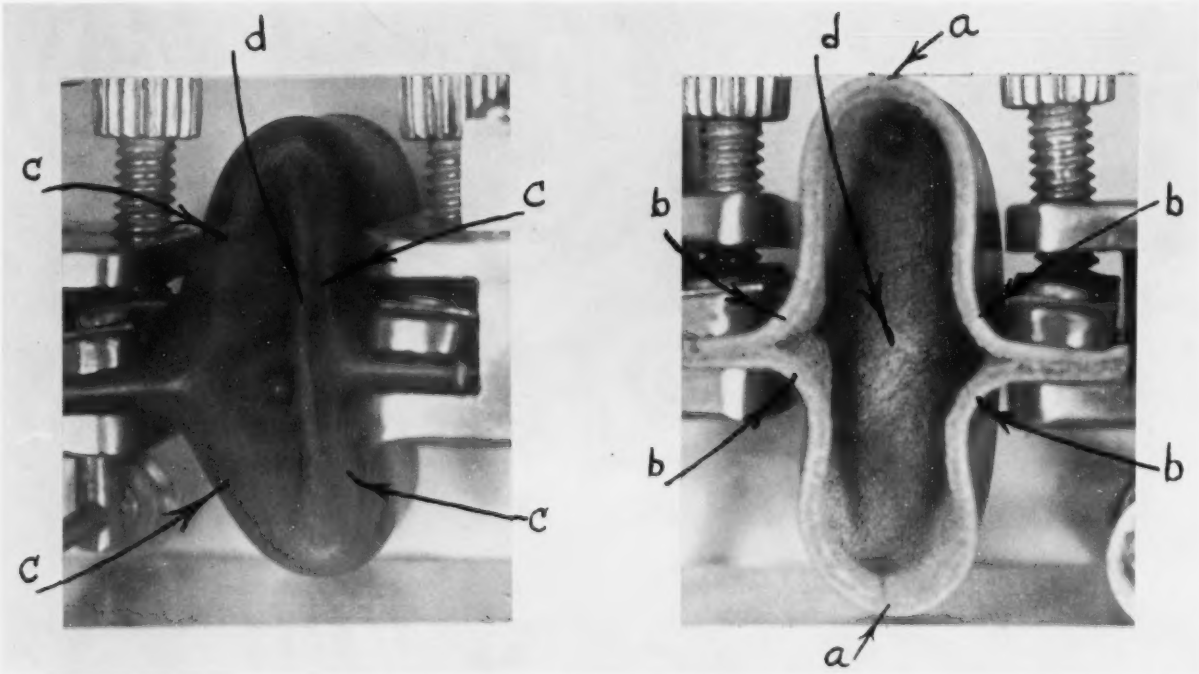

FIGURE 3.—Front and back views of fully cupped specimen. Left, front view showing grain side; right, back view showing flesh side, inside of cup. See Table I for significance of letters designating the different types of fold.

the tests, unless otherwise stated, the specimens were inserted with the head-to-tail, or backbone, direction perpendicular to the direction of travel of the push rod. Thus, when the specimen is flexed, the major folds are parallel to the backbone direction (see Figure 3 and Table I). This, in general, coincides with the condition existing in the vamp of a shoe.

TABLE I

DESCRIPTION OF FOLDS PRODUCED IN CUP FLEX TEST

(*See Figure 3*)

Leather folded grain side out, backbone direction perpendicular to direction of flexing. Cupped from 50 mm. to 20 mm. Specimen 2 7/8″ square.

Location of Folds in Cupped Specimen	Top and Bottom	Clamp Edges	Diagonal	Center
Designation (Fig. 3)	a	b	c	d
Number of folds	2	4	4	1
Direction of fold line in relation to backbone	Parallel	Parallel	Diagonal	Parallel
Type of fold	Convex	Concave	Convex	Concave
Approximate radius of fold	1 mm.	4 mm.	2 to 5 mm.	2 to 3 mm.
Angle of fold	180°	100°	180°	180°
Length of fold lines*	1.4″	5.4″	5.1″	1.5″

*Total length of fold lines is 13.4″, or 27 times the length of the fold line for ½″ specimen used in standard stiffness test.

TABLE II

COMPARISON OF RESULTS OBTAINED BY FLEXIBILITY GAUGE (CUPPING TEST) AND BY A.L.C.A. TEST FOR STIFFNESS

Kind of Leather	Direction of Thrust or Cut of Strip in Relation to the Backbone	Thickness (inches)	Flexibility Gauge* Force in Ounces 1st Flex	Flexibility Gauge* Force in Ounces 20th Flex	Flexibility Gauge* %R	A.L.C.A. Stiffness Test† Force in Ounces 1st Flex	A.L.C.A. Stiffness Test† Span (inches)	A.L.C.A. Stiffness Test† Force calculated to ½″ span
Heavy retan	Parallel	0.103	400	288	72	3.2	1	12.8
Military retan	Perpendicular	0.090	224	156	70	2.02	1	8.06
	Parallel	0.090	244	172	71	2.63	1	10.53
Elk side	Perpendicular	0.072	86	68	79	2.64	0.5	2.64
	Parallel	0.022	71	62	87	1.92	0.5	1.92
Glove horsefront	Unknown	0.048	3.0	2.4	80	0.32	0.25	0.08

*2 ¾″ squares, grain out, flexed from 50 to 20 mm.
†1½″ x 4″ strip, grain convex.

When pressure is applied to the hand knob, the two clamps are forced together, and the upper and lower layers of the folded leather separate, forming a cup (Figures 2 and 3). The stop (*M*, Figure 2) is set so that the clamps are 20 mm. apart at the fully cupped position. This produces folds of about the maximum sharpness likely to be encountered in actual use of the leather, though obviously the sharpness of the folds in a shoe depends on many factors, including thickness and type of leather, size, width, and design of the shoe, conditions of use, and the wearer's walking habits. An analysis of the folds, as illustrated in Figure 3, is given in Table I. The total length of all the fold lines is about 27 times that of the single fold obtained when a ½″ strip is tested by the A.L.C.A. method for determining stiffness (1).

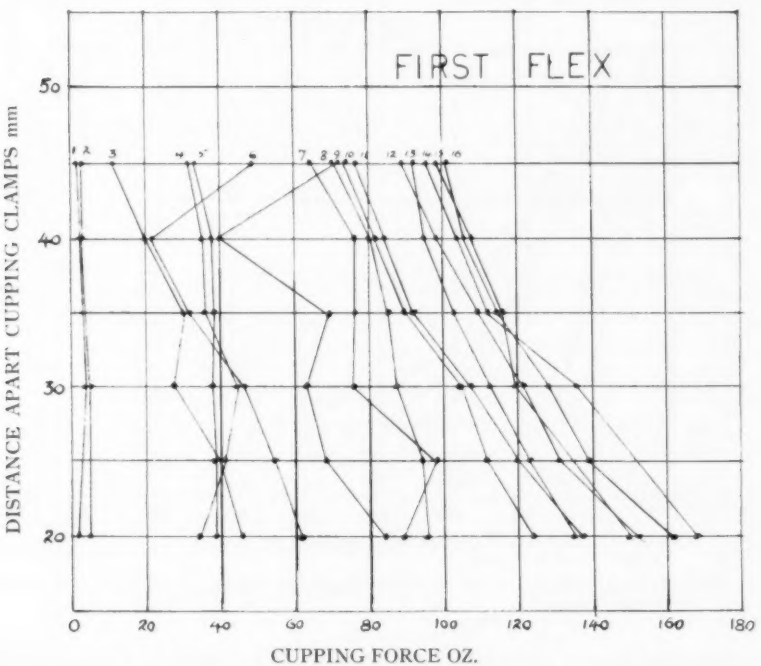

FIGURE 4.—Initial flex forces for various degrees of cupping: 1, glove, horsefront (0.048″); 2, glove, chrome split (0.060″); 3, sheep, vegetable (0.066″); 4, calf A, near belly (0.047″); 5, calf A, near backbone (0.049″); 6, elk side (0.070″); 7, calf B, near shank (0.050″); 8, elk side, silicone-waterproofed (0.075″); 9, military retan upper, shoulder near backbone (0.075″); 10, same, with organic waterproofing agent (0.082″); 11, military retan upper, bend near backbone (0.091″); 12, military chrome upper, C, fatliquored (0.086″); 13, same, D (0.090″); 14, special retan side upper (0.100″); 15, military retan upper (0.082″); 16, military fatliquored chrome upper, degreased (0.090″).

Because of the multiple folds and the comparatively large area of the specimen, the test gives results that well represent the piece of leather tested. A comparison of results obtained on adjacent specimens by the cupping method and by the A.L.C.A. method using a Tinius Olsen tester is given in Table II.

The force required to cup the specimen depends on the degree of cupping, i. e., the distance between the clamps and the end of the stroke. Curves illustrating this are given in Figures 4 and 5.

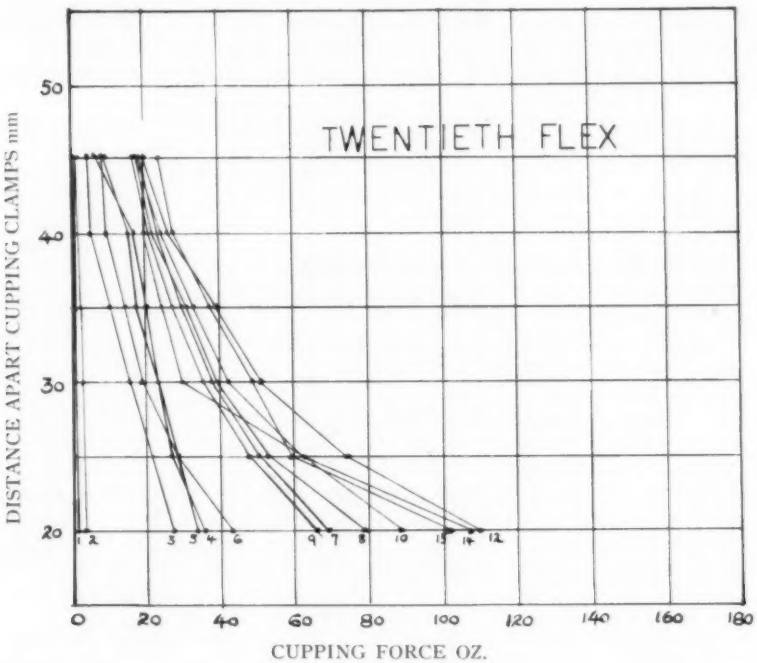

FIGURE 5.—Twentieth-flex forces for various degrees of cupping; same leathers as shown in Figure 4.

For reasons to be given later, it is desirable to measure the force required to cup the specimen for the first time and also the force required after the specimen has been flexed a considerable number of times (usually 20). The method for carrying out such a test is as follows:

The swivel arm is set so that the minimum distance between the clamps will be 20 mm., and the arm is turned down. The hand knob is pushed steadily and uniformly so that the flex is completed in about 7 seconds. The force applied is read from the dial. The knob is drawn back to the original

position, and the specimen is flexed rapidly 18 times (one second per flex), ordinarily without reading the dial. Then the twentieth flex is made just like the first and the dial read again.

This procedure, using a 2 7/8" square cupped to 20 mm., can be used for a wide variety of leathers and other materials. The useful range of the apparatus can be extended by varying the size of the specimen or the degree of cupping. For very flexible materials a smaller specimen is desirable in order to obtain dial readings of at least several ounces, because the folds are smaller and the force required is greater as the specimen size is reduced. Table III contains some examples of leathers and other materials that were tested with a 1 3/4" x 2 7/8" specimen folded and inserted with the 1 3/4" dimension in line with the push rod. The initial distance between the clamps

TABLE III

TYPICAL RESULTS OF CUP FOLD TESTS

REGULAR TEST SPECIMENS, 2⅞" SQUARE CUPPED FROM 50 TO 20 MM.					VERY FLEXIBLE SPECIMENS, 1¾"x2⅞" CUPPED FROM 25 TO 15 MM.			
Material	Location*	Thickness (inches)	Force (ounces) for 20th Flex	% R	Material	Thickness (inches)	Force (ounces) for 20th Flex	% R
Side Leathers:					Kid garment	0.039	4.3	78
Specimen A	BB	0.0675	70	83	Glove:			
A	Belly	0.068	75	81	Horsefront	0.048	4.7	80
B	BB	0.069	81	81	Cowhide	0.056	3.2	76
B	Belly	0.070	63	81	Buckskin	0.076	5.9	75
Black calf	BB	0.049	40	88	Chrome:			
	Belly	0.048	34	78	split A	0.057	4.6	85
Tan calf	BB	0.044	31	75	split B	0.053	3.1	68
Military retan	BB	0.096	136	71	Twill canvas:			
Same, degreased	BB	0.088	94	75	crosswise	0.020	2.8	76
White elk	BB	0.067	36	75	lengthwise	0.020	5.0	74
	Belly	0.066	52	72	"Leatherized" cloth	0.015	4.5	70
Sheepskin, comb. tan, finished	BB	0.053	30	70	Oilcloth	0.012	1.8	51
Sheepskin, veg. tan, unfinished	BB	0.051	22	73	Upholstery fabric	0.021	8	40
Rawhide lace	——	0.058	12	60				
Inner tube	——	0.119	44	100				

*"BB" means a location near the backbone; "Belly" means a location near the belly.

was 25 mm., and the specimens were cupped to 15 mm. A lighter spring reading to 0.1 ounce was used for these measurements. Often, on very flexible and thin materials, the uniform cupping fold pattern does not form unless a slight pressure (finger or end of a pencil) is applied at the center of the folded-over edge where the center vertical fold starts to form.

For very stiff, heavy materials, the specimen size may be increased or the degree of cupping lessened. An example of a test where such modification might have been desirable is the heavy, 0.103″-thick retan leather in Table II. The first flex for this leather produced some crowding of the folds, and the force required (400 ounces) appears to be out of line with other results. Such a leather would be used only in large-size, heavy-type shoes, where the folds produced in use would be less sharp than with lighter leathers. For such leathers, cupping from an initial apart-distance of 50 mm. to a final distance of 25 mm. or even 30 mm., instead of the standard 20 mm., might be preferable.

Obviously, specimens of a given type or kind of leather should always be tested under identical conditions, and no attempt should be made to compare results obtained under different conditions.

RESULTS AND DISCUSSION (CUPPING TEST)

Effect of Repeated Flexing.—As already mentioned, the force required to flex a specimen is measured for the first flex and also for the twentieth flex. There are three reasons for this: First, the force measured on the first flex is somewhat irregular. Figures 4 and 5 give the forces required to cup specimens to different degrees on the first and twentieth flexes respectively. The curves obtained on the twentieth flex are much smoother. Second, the force required to cup the specimen declines with repeated flexing but appears to become nearly constant at or before the twentieth flex (Figure 6). Third, the change in resistance to flexing between the first and twentieth flexes is related to resilience, which is a factor in the subjective property known as "temper".

Temper Characteristics.—J. A. Wilson (2) described temper as being that quality of light leather which is judged by running the hand along a folded side or skin and noting vigor of rebound upon release of pressure. He considered the two components of temper to be flexibility and recovery and devised tests for measuring these components. In addition, it is felt that thickness, aside from its effect on flexibility, is an inherent factor in temper and feel. The three major factors in temper are thus thickness, flexibility, and resilience.

The force required to flex a specimen decreases on repeated flexing because of movement of fibers, creeping of the structure, piping on the concave side, etc. After 20 flexes, most of these changes have occurred. The ratio of the

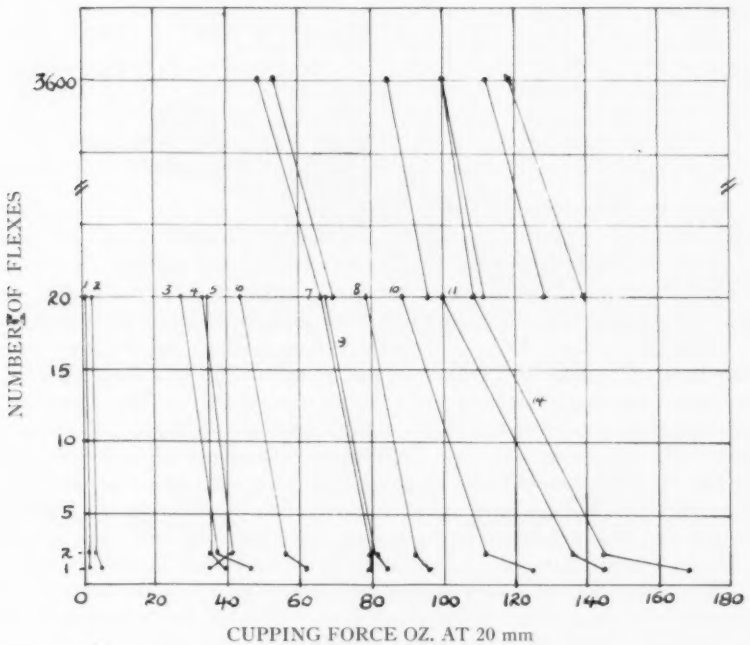

FIGURE 6.—Changes in flex force with number of flexes; same leathers as shown in Figure 4. Flexed perpendicular to backbone from 50 mm. to 20 mm.

flex force for the twentieth flex to the flex force for the first flex, expressed as a percentage of the latter, appears to be one method of expressing resilience. This ratio (% *R* in Table II and following tables) has been selected as the means of determining resilience in tests made with this gauge.*

The following measurements made on two retan sides illustrate this method for evaluating temper. One side had been dried without stuffing; the other had been stuffed to contain about 21% grease. Specimens were cut from similar locations, and the flex forces were determined for the first and twentieth flexes. The average thicknesses of the test specimens, the forces required for the twentieth flex**, and the ratios of the twentieth-flex forces to the initial-flex forces are given below.

*In mechanics, resilience generally is used to express the potential energy of recovery. A material which recovers a long distance under a low force may have the same resilience as another which recovers only a small distance under a high force. The procedure used by the author is not a direct measure of resilience. However, a material that retains a high percentage of its initial resistance to flexure after having been flexed repeatedly would appear to possess greater resilience than one which loses most of its resistance to flexing. Thus the use of the fraction *R* as a qualitative index of resilience appears to be justified.—*Editor.*

**Since the test specimens differed slightly in thickness, the values for the twentieth-flex force were adjusted to the average thickness on the assumption that the force varied directly as the cube of the thickness.

	Av. Thickness (inches)	% R	20th - Flex Force (ounces)
Unstuffed piece	0.090	84	211
Unstuffed piece	0.090	79	200
Stuffed piece	0.090	71	111

The unstuffed piece was bony, tinny, and harsh-feeling. This correlates with the much higher values for the flex force. A leather of this thickness giving such a high flex force is thus firm and stiff. The resilience of the unstuffed side is high. On the other hand, the resilience, *R*, of the stuffed side is low, compared with normally fatliquored leathers that contain less grease.

Table III contains the same data for various leathers and for some other materials. First-flex force values are not given but can be calculated by dividing the twentieth-flex force by % *R* and multiplying by 100. These tests indicate that the procedure gives results having the degree of accuracy needed for evaluating flexibility. Differences in flexibility scarcely detectable by feel can be measured easily by the gauge. In general, the tests show that mineral-tanned leathers have higher resilience than vegetable-tanned leathers. Leathers of high grease content generally show low resilience. The low resilience of plastic materials and the 100% resilience of rubber are obvious.

The results obtained vary with the direction in which the specimen is cupped (with respect to the backbone line). Usually, but not always, the flex force is greater when the backbone direction is parallel to the direction of travel of the push rod. This directional effect is shown also by the specimen of twill canvas. Resilience varies considerably for different locations in the piece of leather. For this reason the location of the test specimen should always be stated, and tests must be made on specimens from several locations to arrive at a fair estimate of the resilience of the piece.

The resilience figures reveal differences between leathers that differ in feel, as assessed by handling. Resilience is a measure of the springiness of leather and is closely allied to the degree of recovery of the leather after bending. These properties are not, however, exactly the same. Other factors, such as the evenness and sharpness of bend, have a bearing on the feel of the leather.

TESTING HEAVY LEATHERS (STRIP BENDING TEST)

The modified apparatus, as used for testing heavy leathers, is illustrated in Figure 7. A metal plate, 1½″ x 3½″, is attached to the push clamp. This plate supports two posts, 3″ apart and equidistant from the center line of the apparatus. A washer and a loosely fitting sleeve are slipped over each post; the washers hold the lower edge of the test specimen clear of the plate, and the sleeves minimize friction between the specimen and the posts. A scale for measuring the degree of bend is engraved on the plate (Figure 8).

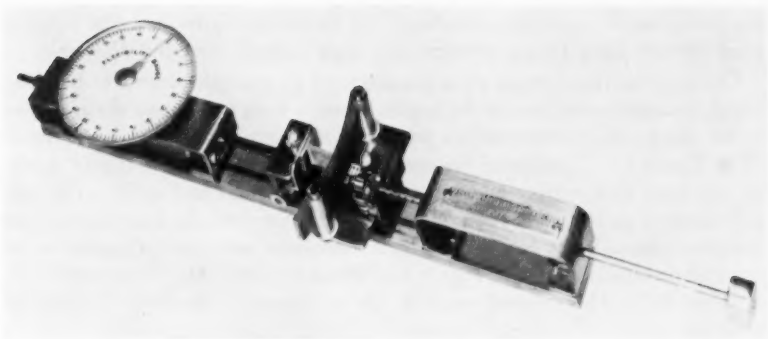

FIGURE 7.—Flexibility gauge as used for strip bending test.

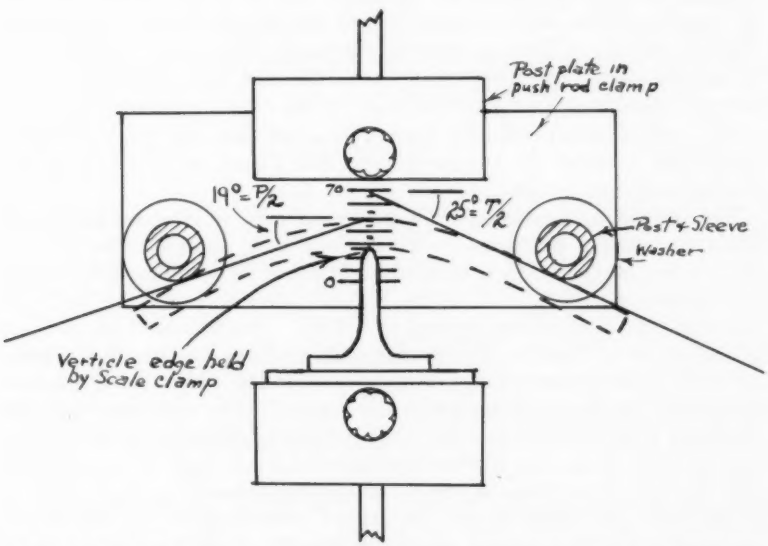

FIGURE 8.—Sketch showing details of strip bending test, top view. The broken lines show the position of the strip bent to the tangent angle of 50°.

A small metal plate carrying a projecting bar with a vertical edge about 5/8″ long is fastened to the scale clamp.

The test specimen, usually a strip 4″ x 3/4″ cut parallel to the backbone, is placed on edge with the grain side against the posts. When force is applied to the push knob, the vertical edge mounted on the scale clamp presses against

the center of the specimen, bending it as shown in Figure 8. The force to bend the specimen to a predetermined angle is read from the dial scale.

The scale on the support plate is calibrated to show the degree of bending, which is taken as the sum of the angles between lines tangent to the specimen at the posts and a horizontal line forming a right angle with the axis of thrust ($T/2$, Figure 8). The sum of these angles is referred to as the Tangent Angle, T. All tests were performed by bending the specimens to $T=50°$. The tangent angle is greater than the sum of the angles between the lines drawn from the posts through the front of the bent specimen and a line tangent to the front of the specimen ($P/2$, Figure 8). When $T=50°$, this "Post Angle", P, is about 38°. The tangent angle is felt to represent the true amount of bending.

The technique of the measurements is similar to that used in the cupping test. The force required for the first bend is measured. When the force is released, the strip straightens out partially. The bending is repeated rapidly 18 times, and then the force required for the twentieth bend is measured. The twentieth-bend force is taken as a measure of flexibility, and the ratio of the twentieth- to the first-bend force, expressed as a percentage of the latter, is taken as a measure of resilience (% R).

The point to which the bent specimen returns after the twentieth flex is noted; this is called the Degree of Set. The Degree of Recovery is then 50° minus Degree of Set.

The range of application of the bending test may be increased by making changes in the test conditions similar to those made in tests with the Tinius Olsen tester in the A.L.C.A. Method for Stiffness E43. For example, with very flexible materials, such as the ½″-wide welting leather in Table IV, the inter-post distance was reduced to 1 3/4″. This increased the force required for the 50° bend to a value that could easily be read on the dial scale. In other cases it might be desirable to decrease the width of the specimen or to bend it to a tangent angle different from 50°. The same test conditions should be used whenever possible when comparing similar materials. When this is not possible, the relationships between force, angle of bend, width and thickness of specimen, and span (inter-post distance) as given in A.L.C.A. Method E43, paragraph 5, may be applied, with reservations. In theory, the bending force for a given material is directly proportional to the width of the strip, to the angle of bend, and to the cube of the thickness, and inversely proportional to the square of the span. Not all these relationships apply exactly to leather. Tests were made in which angle of bend, width, thickness, and inter-post distance were varied. The force required to bend a piece of sole leather to 50° is less than twice the force required to bend it to 25° because of the permanent set that takes place when the elastic limit is exceeded. In one test, the forces required to bend a strip to 15, 30, and 45° were 41, 67, and 85 ounces respectively. Similar results were obtained with

TABLE IV

BENDING TESTS ON HEAVY LEATHERS AND COMPOSITION MATERIALS
EFFECTS OF TEMPERATURE (°F.)

Material	20th-Flex Force (Ounces)				% Resilience			Degrees of Set		
	32°	73°	100°	% change 32 – 100°	32°	73°	100°	32°	73°	100°
*Oak sole, 11–12 iron:										
Tannage A	120	125	110	8	84	86	88	12	12	17
Tannage B	146	152	136	7	76	81	82	15	14	17
*Chrome sole, filled, 12 iron	222	197	123	45	71	72	68	20	21	23
*Same, degreased		82				82			16	
*Chrome sole, filled 8 iron	134	76		58	75	60	47	12	17	16
*Same, degreased		34				92			3	
*Composition soles:										
7 iron	39	30			74	75		14	16	
9 iron	78	54	46	41	74	73	70	14	15	21
12 iron	114	79			69	66		14	16	
11 iron (low grade)	39	28			81	85		9	8	
*Belting:										
Oak, single, 8 iron		12				92			21	
Rubber-canvas, 9 iron		17				85				
*Insole material:										
Cellulose fiber. 2½ iron		7				85			11	
†Welting:										
Leather, concave, 0.122″		11				89			15	
Plastic, rib convex, 0.128″		20				80				

*Strips 4″ x ¾″ cut parallel to backbone; post distance 3″; 50° bend; grain convex.
†Strips ½″ wide; post distance 1¾″; bent as indicated.

the Tinius Olsen tester. Doubling the width of the strip more than doubles the force required, probably due to edge effects that are more prominent for narrow specimens. Tests on composition sole materials showed that the bending force was substantially proportional to the cube of the thickness, but since leather varies in structure between grain and flesh, and since the ratio of grain layer to flesh layer varies from one leather to another, it is evident that the theoretical relationship cannot apply exactly. The amount of deviation from the theoretical relationship probably depends on the thickness and type of leather and degree of bending. For composition materials, not bent beyond the elastic limit, the bending force came close to

being inversely proportional to the inter-post distance. However, as the inter-post distance decreases, so does the radius of curvature, and with heavy leathers movement of fibers and permanent set occurs at a relatively low degree of bend. The inverse relationship between bending force and inter-post distance was found to apply over a limited range only and is only approximate for the standard 50° angle of bend.

RESULTS OF STRIP BENDING TESTS

Tables IV, V, and VI contain some results obtained by the strip bending test and illustrate its use for determining the effects of various conditions and treatments on flexibility, resilience, and degree of set. Table IV contains results of tests made at different temperatures (32°, 75°, and 100°F.). It is interesting to note that vegetable sole leather is less affected by temperature,

TABLE V

BENDING TESTS ON SOLE LEATHERS EFFECTS OF MOISTURE

Strips 4″ x 3/4″ cut parallel to backbone; post distance 3″ ; 50° bend; flex forces corrected to average thickness of sole leather samples. Adjacent specimens used for dry and wet tests.

Material	20th-Flex Force (ounces)				% Resilience			Degrees of Set		
	Dry	Soaked 24 hr.	Conditioned at 95% RH	Ratio Dry/Wet	Dry	Soaked 24 hr.	Conditioned at 95% RH	Dry	Soaked 24 hr.	Conditioned at 95% RH
Oak sole, 11–12 irons, strips from bend:										
Tannage B, belly end	118	13	76	9	69	75	77	10	40	23
	164	12	38	14	64	75	67	12	40	17
	128	2.5	62	51	67	55	79	17	35	22
Tannage B, backbone end	138	16	57	9	75	76	77	12	40	23
	102	17	43	6	77	80	78	17	44	28
	88	16	44	5.5	75	81	78	18	42	26
Tannage C, belly end	141	5	85	28	80	75	75	18	42	20
	95	1	100	95	83	50	78	12	35	20
			120				78			17
Tannage C, backbone end	70	12	67	6	74	82	88	22	33	24
	97	16	68	6	82	77	81	27	35	20
			119				88			18
Retan insole, 7½ iron	18	13		1.4	97	88		7	8	

TABLE VI

BENDING TESTS ON SOLE LEATHER VARIOUSLY TREATED

First figure, Tannage A; second figure, Tannage B. Strips 4″ x ¾″ cut parallel to backbone; post distance 3″; 50° bend; grain convex; 20th-flex force corrected to average thickness.

Treatment	20th-Flex Force (ounces)					% Resilience			Degrees of Set			% Weight Gain	
	Dry	Soaked 1 hr.	Soaked 24 hr.	Re-dried	Ratio dry/24 hr. soak	Dry	Soaked 24 hr.	Re-dried	Dry	Soaked 24 hr.	Re-dried	Soaked 1 hr.	Soaked 24 hr.
Conventional heavy mineral oil	136	64	8	82	17	78	50	84	7	35	12	17	38
	165	38	7	90	24	64	47	77	9	48	13	18	45
Isobutylene polymer*	114	32	11	60	10	77	65	70	9	33	20	9	23
	159	30	7	78	21	68	50	72	10	44	15	14	26
Special waterproofing compound	115	77	31	64	4	73	71	77	11	32	21	4	20
	165	83	29	65	6	62	71	70	13	35	19	4	21
Resin plasticizer*	165	74	31	77	5	66	55	65	23	34	21	6	26
	157	57	20	74	8	61	50	66	20	39	20	7	31
Commercial silicone*	113	51	30	61	4	81	61	78	9	28	13	6	28
	126	48	34	66	4	79	66	79	11	28	14	6	29
Chrome retannage†	88	22	25		3.5	75	85	70	10	16		35	35
	132	46	62		2	80	70	82	10	20		31	32
Formaldehyde retannage†	87	36	43		2	75	92	88	10	14		42	43
	134	62	70		2	79	82	85	10	19		37	38
No treatment	99	10	9	83	11	79	72	77	14	39	12	29	49
	168	15	5	92	32	81	62	76	12	44	15	24	48

*Added to finished leather in 50% solvent solutions to add approximately 8% material to the leather.
†Retanned for 2 days.

and has higher resilience, than filled chrome sole leather or composition sole material. Table V contains results for dry leathers, leathers soaked for 24 hours, and leathers exposed to 95% relative humidity. It is very evident that vegetable sole leather is greatly affected by moisture content; the retan insole leather much less so. The ratio of the dry to the wet flex force may prove a useful index of leather quality, reflecting differences in fiber structure, fiber solidity, content of water solubles, etc. This ratio is higher for loose-fibered specimens. While no data are given for belly and shoulder locations, these probably would have given still higher values. It will be noted that specimens cut near the belly edge of the piece actually are firmer in the dry state than pieces cut near the backbone. After soaking, the reverse is true, and the ratio of dry to wet firmness is much higher for the belly edge specimens. Tests of this sort are very easy to make and may serve as a guide to sole leather quality.

Table VI shows the effects of various treatments applied to sole leather. The conventional waterproofing treatment with heavy mineral oil does not protect the leather appreciably from water, judging from the ratio of dry to wet flexibility. The percentage gain in weight due to water pickup, corrected for water solubles and oil removed by the soak, is given to afford a comparison between change in flexibility and water pickup. The other treatments show various effects. For most of them, the ratio of dry to wet flexibility was much lower than for the untreated leather. Retannage with aluminum and with zirconium compounds (data not shown) had about the same effect as retannage with chromium.

One comparison was made between results obtained with the flexibility gauge and with the Tinius Olsen stiffness tester, using adjacent strips of oak, sole leather ½″ wide and 0.220″ thick. On the gauge, the first bend to 50° with the posts 3″ apart required a force of 84 ounces. On the Tinius Olsen instrument, a 25°-bend with 3″ span required 32.2 ounces.

SUMMARY

1. A simple, rugged, and inexpensive instrument for measuring the force required to bend or flex leather is described. A slight modification of the instrument permits its use for heavy as well as light leathers.

2. The force required to bend or flex a leather specimen decreases on repeated flexing but becomes nearly constant after about 20 flexes. The twentieth-flex force is taken as a measure of stiffness, which is the converse of flexibility, and the ratio of the twentieth-flex force to the first-flex force is taken as a measure of resilience, which is a factor in temper.

3. Data are given that illustrate the use of the instrument for measuring the flexibility and resilience of leathers of various types, and for studying the effects of various treatments on these properties of leather.

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DO WE NEED AN INDUSTRIAL WASTE FOUNDATION?

The water problem in the United States becomes more serious with each passing day. Municipalities and industry to an ever-increasing extent must depend upon our streams and rivers. This means, of course, a rational control of pollution, in an era when there will be a much larger population and a huge upward surge in manufacturing. Unless much scientific progress is made quickly, the situation undoubtedly will become much worse as the economy continues to expand.

Many experts in the field agree that the most acute need is for a great expansion in fundamental research. We must know much more about the fundamental reactions that occur in streams if we are to use them properly.

One of the 1956 Gordon Research Conferences was on the theme: "Scientific Bases for Water Quality Control". The general conclusion was that there is not yet enough scientific knowledge available to propose sound criteria, except in a few instances and to a limited extent. This state of affairs is discouraging. Yet the chemical industry alone is spending $40 million annually for pollution control. Industry is not sitting on its hands in this matter, though much more needs to be done.

A year or two ago, a proposal was made by Richard D. Hoak of Mellon Institute that an industrial wastes foundation be established. He mentioned how a foundation could serve a variety of needs, of which fundamental research on water pollution would be a significant one. He stated that the need for an organized program of fundamental research on water pollution arises from (1) a serious lack of dependable data upon which to base control measures, (2) predictions of greatly increased demand for industrial water over the next 20 years, (3) a growing necessity for conservation of water through reuse, and (4) a clear indication that waste treatment requirements will become increasingly stringent.

The exploration of ways and means of creating an industrial waste foundation seems particularly pertinent at this time.

—Excerpts from an editorial by Walter J. Murphy in *Chemical and Engineering News*, December 10, 1956. Reprinted by permission.

In 1860, tanneries were dispersed throughout the country and ranked fifth among all industries in the number of establishments . . . The New England and Middle Atlantic States imported substantial quantities of hides, and their capacity averaged three times that of tanneries in the South and West. In 1858, 1,075,000 hides were imported to augment domestic supplies of raw material.

—*Economics of Cattlehide Leather Tanning.* Merrill A. Watson, D.C.S. Chicago: The Rumpf Publishing Company, 1950.

INFLUENCE OF TEMPERATURE ON THE REACTION OF A CHROME TANNING SOLUTION WITH CALFSKIN SQUARES

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ABSTRACT

The influence of temperature on chrome tanning is of interest because the data may be used to calculate heats of reaction and to obtain fundamental information on the mechanism of tanning. The procedure used was to soak 2 grams of dry-dehaired, delimed hide in water until fully swollen and then add varying amounts of chromium from a 33⅓% basic, SO_2-reduced, tanning agent. Determinations of hide substance, chromic oxide, and total sulfate were made on the washed, tanned squares. Under all conditions the amount of chromic oxide (Cr_2O_3) retained at 50° C. was 3 to 4 times greater than that retained at 0° C. Addition of formic acid decreased the amount retained at all temperatures. From the data obtained at different temperatures, it was found that the combined chrome complex had an acidity of about 41%. The amount of protein-bound acid was found to be a constant at about 0.39 milliequivalents per gram of collagen.

The effect of increasing temperature on chrome tanning is explained by increased hydrolysis, accelerated by an increase in the ionization constant of water, to form larger chrome complexes.

INTRODUCTION

Since temperature increases the rates of nearly all chemical reactions, it is expected that it might also increase the rate of tanning. Tanning reactions are, however, more complex than most chemical reactions since a number of physical processes are involved. In chrome tanning, the additional factor of complex formation, which is accelerated by increase in temperature, is important. Rate of diffusion also increases with a rise in temperature. Combination of protein with acids (1) changes little with temperature, and adsorption of water decreases with increase in temperature. The influence of temperature on chrome tanning will, therefore, be a summation of these various factors.

One important paper on the subject of the effect of temperature on chrome tanning is the work of Merrill and Schroeder (2). The work given in this paper agrees in all important respects with their results and indicates the importance of close control of temperature in chrome tanning for the continuous production of leather having uniform properties.

In addition to the practical results, the present paper gives an analysis of the data to determine the ratio of chromium (expressed as Cr_2O_3) to sulfate (expressed as H_2SO_4) in the chrome tanning complex. A study is made of the protein-bound acid, and calculations of the heats of reaction of the chrome complex are made.

PROCEDURE

The raw hide used in these studies was prepared from a limed and unhaired calfskin. The skin was cut into squares approximately ½″ x ½″. The squares were mixed at random, washed thoroughly with water to remove lime and soluble proteins, and dehydrated with acetone.

Two grams of the dehydrated calfskin squares were placed in water and permitted to come to a steady state of swelling. Varying amounts of a conventional one-third basic* sulfur dioxide–reduced chrome tanning solution,† diluted to 200 ml. in each case, were then added. Experiments were made with the original chrome tanning solution with and without the addition of varying amounts of formic acid (reagent grade). These test solutions were placed in a water bath controlled to ±0.1° C. The flasks were shaken intermittently during the tanning.

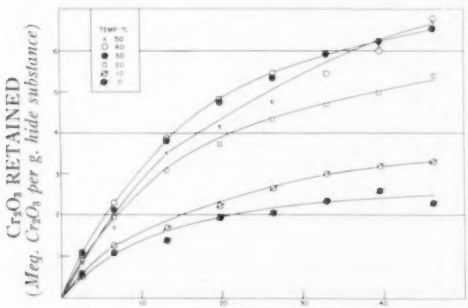


FIGURE 1.—Influence of temperature on the increase in the retention of chromium by calfskin squares with an increase in the concentration of chromium in the chrome tanning solution. Liquors contained 0.06 *M* formic acid.

*The basicity is the ratio of hydroxyl OH in milliequivalents to milliequivalents of chromium in the chrome tanning solution.

†A typical chrome tanning solution of this type may be obtained by adding 3 moles of sulfur dioxide to 1 mole of potassium dichromate in aqueous solution:

$$K_2Cr_2O_7 + 3\ SO_2 + H_2O \longrightarrow K_2SO_4 + 2\ CrOHSO_4$$

The reduced chrome tanning solution is allowed to age for a suitable length of time before it is used.

Experiments were made at temperatures in 10° steps ranging from 0° to 50° C., and the time of tanning was 96 hours. After tanning was completed, the liquor was poured off, and the tanned squares were washed in three changes of distilled water for about five minutes each to remove occluded chrome tanning solution from the surface of the squares. Coloration of the washing solution was noticeable only in the first wash. The squares, after washing, were dried in air and room temperature and finally at 100° C. to remove all moisture. Hide substance and chromic oxide were determined on the tanned squares in accordance with Methods 6461 and 6515, respectively, of Federal Specification KK-L-311a (3). Sulfates were determined by oxidizing the tanned leather with a mixture of perchloric acid and nitric acid and then proceeding in accordance with Method 6361 in KK-L-311a, starting with paragraph 4.3.

RESULTS

The retention of the chrome complex by calfskin squares tanned in chrome solutions varying in chromium content and containing 0.06*M* formic acid,

TABLE I

INFLUENCE OF TEMPERATURE ON THE RETENTION OF CHROMIUM BY THE HIDE SUBSTANCE OF CALFSKIN SQUARES TANNED IN SOLUTIONS CONTAINING VARYING AMOUNTS OF CHROME TANNING AGENT AND 0.06 *M* FORMIC ACID

Concentration of tanning solution Meq. Cr_2O_3 in 200 ml.	Meq. Cr_2O_3 Retained by 1 g. Collagen					
	0°C.	10°C.	20°C.	30°C.	40°C.	50°C.
2.6	0.6	0.5	0.9	1.1	1.0	0.8
6.6	1.1	1.3	1.9	2.1	2.3	1.7
13.2	1.4	1.7	3.1	3.8	3.8	3.5
19.8	1.9	2.2	3.7	4.8	4.8	4.1
26.4	2.0	2.6	4.3	5.3	5.5	4.7
33.0	2.3	3.0	4.7	5.9	5.5	5.9
39.6	2.6	3.2	5.0	6.2	6.0	6.1
46.2	2.3	3.3	5.4	6.5	6.8	6.7

is shown in Figure 1 and Table I. The pH values of these solutions varied from 3.36 to 4.12. Some form of chromium was precipitated from the solutions at the higher temperatures. The amounts and compositions of chromium compounds precipitated at 40° and 50° C. is shown in Table II. The amounts precipitated at 30° and 20° C. were less than 20 mg. and 11 mg. respectively. Determination of the Cr_2O_3 content of the precipitates at 40 and 50° C. indicated that the compound corresponds to the composition of the one-third basic salt $[Cr_2(OH)_2(SO_4)_2]$. Retention of chromium increases with each increase in temperature from 0° to 30°C. At temperatures

of 30° to 50°C. the retention of chromium appears to have reached a maximum of approximately 6.0 milliequivalents per gram of hide.

TABLE II

ANALYSIS OF THE PRECIPITATE FROM TANNING SOLUTIONS

40° C.				50° C.			
Wt. of ppt. g.	Cr_2O_3 g.	Cr_2O_3 %	Wt. of ppt. / Cr_2O_3	Wt. of ppt. g.	Cr_2O_3 g.	Cr_2O_3 %	Wt. of ppt. / Cr_2O_3
.0244	.0116	47.5	2.10				
.0421	.0194	46.1	2.17	.0777	.0365	47.0	2.13
.0568	.0275	48.4	2.07	.1273	.0574	45.1	2.22
.0584	.0276	47.3	2.12	.1558	.0738	47.4	2.11
.0590	.0289	49.0	2.04	.1666	.0730	43.8	2.28
.0514	.0245	47.7	2.10	.1642	.0748	45.6	2.20
.0402	.0188	46.8	2.14	.1651	.0765	46.3	2.16
.0297	.0131	44.1	2.27	.1455	.0679	46.7	2.14
Average		47.1	2.13			46.0	2.18

Cr_2O_3 in $Cr_2(OH)_2(SO_4)_2 = 46.1\%$

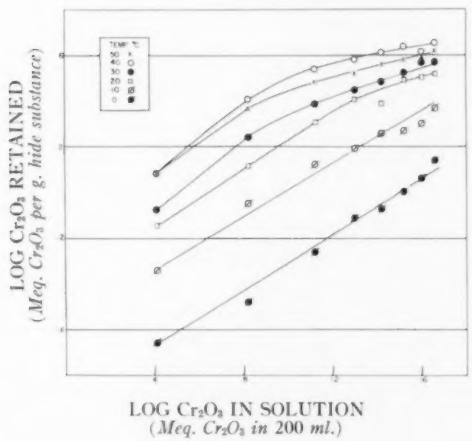


FIGURE 2.—Influence of temperature on the retention of chromium by calfskin squares with an increase in the concentration of chromium in the chrome tanning solution. Liquors contained 0.12 *M* formic acid.

In Figure 2 the logarithm of the amount of chromium retained after tanning, expressed as Cr_2O_3, is plotted against the logarithm of the concentration (milliequivalents of Cr_2O_3 in 200 ml.) of the tanning solutions which

TABLE III

INFLUENCE OF TEMPERATURE ON THE RETENTION OF CHROMIUM BY THE HIDE SUBSTANCE OF CALFSKIN SQUARES TANNED IN SOLUTIONS CONTAINING VARYING AMOUNTS OF CHROME TANNING AGENT AND 0.12 *M* FORMIC ACID.

Concentration of tanning solution Meq. Cr_2O_3 in 200 ml.	Meq. Cr_2O_3 Retained by 1 g. Collagen					
	0°C.	10°C.	20°C.	30°C.	40°C.	50°C.
2.6	0.2	0.5	0.7	0.8	1.2	1.2
6.6	0.3	0.9	1.3	1.7	2.6	2.3
13.2	0.5	1.3	2.0	2.5	3.5	3.1
19.8	0.8	1.6	2.6	2.8	3.8	3.3
26.4	0.8	1.8	2.5	3.1	4.1	3.7
33.0	1.0	1.9	3.1	3.4	4.4	3.8
39.6	1.1	2.0	3.2	3.7	4.1	3.9
46.2	1.4	2.3	3.4	3.7	4.6	4.2

TABLE IV

INFLUENCE OF TEMPERATURE ON THE RETENTION OF CHROMIUM BY THE HIDE SUBSTANCE OF CALFSKIN SQUARES TANNED IN SOLUTIONS CONTAINING VARYING AMOUNTS OF CHROME TANNING AGENT AND 0.6 *M* FORMIC ACID

Concentration of tanning solution Meq. Cr_2O_3 in 200 ml.	Meq. Cr_2O_3 Retained by 1 g. Collagen					
	0°C.	10°C.	20°C.	30°C.	40°C.	50°C.
2.6	0.05	0.1	0.2	0.4	0.6	0.7
6.6	0.1	0.2	0.4	0.6	1.0	1.3
13.2	0.2	0.3	0.6	0.8	1.3	1.6
19.8	0.3	0.5	0.7	1.0	1.4	1.6
26.4	0.3	0.5	0.8	1.1	1.5	1.8
33.0	0.4	0.6	0.9	1.1	1.6	1.8
39.6	0.4	0.7	1.0	1.4	1.6	2.0
46.2	0.5	0.7	1.1	1.4	1.7	2.2

vary in chromium content in the same manner as those for which results are given in Figure 1 and Table I. In this experiment the formic acid content was increased from 0.06 *M* to 0.12 *M*. These results are also shown in Table III. The pH values of the solutions varied from 3.14 to 4.07; no form of chromium was precipitated from these solutions because the amount of formic acid was increased. The amount of chromium complex combined increases with each increase in temperature from 0° to 40° C. Retention of chromium at 50° is actually less than that at 40° C., possibly because a slight shrinkage occurs at 50° before sufficient tanning takes place, or perhaps because of increased formation at the higher temperature of formato-chromium complexes which have lower affinity for hide. The maximum amount of chromium retained by the hide under these conditions is about 4 milliequivalents per gram.

Results of experiments where the formic acid content was increased to 0.6 *M* are given in Table IV. The pH values of these solutions ranged from 2.88 to 3.89. Chromium was not precipitated. The data show that as the temperature is increased the amount of the chromium complex combined, expressed as Cr_2O_3, increased in approximately equal increments for each step in the temperature rise. The maximum amount of chromium retained is, however, only about 2 milliequivalents per gram of hide substance.

The tanned squares for which results are given in Figures 1 and 2 and Tables I, III, and IV were analyzed for chomium only*. Additional experiments were made in which analyses were made also for the amount of sulfate in the leather, expressed as H_2SO_4, and the amount of hide substance. For these experiments a new chrome tanning solution was prepared which contained a slightly higher chromium content.

TABLE V

INFLUENCE OF TEMPERATURE ON THE RETENTION OF CHROMIUM AND SULFATE BY THE HIDE SUBSTANCE OF CALFSKIN SQUARES TANNED IN SOLUTIONS CONTAINING VARYING AMOUNTS OF A CHROME TANNING AGENT AND 0.06*M* FORMIC ACID

Concentration of solution Meq. Cr_2O_3 or H_2SO_4 in 200 ml.	Meq. Cr_2O_3 or H_2SO_4 Retained by 1 g. Collagen											
	0°C.		10°C.		20°C.		30°C.		40°C.		50°C.	
	Cr_2O_3	H_2SO_4	Cr_2O_3	H_2SO_4	Cr_2O_3	H_2SO_4	Cr_2O_3	H_2SO_4	Cr_2O_3	H_2SO_4	Cr_2O_3	H_2SO_4
3.0	0.4	0.4	0.3	0.3	0.7	0.5	1.0	0.5	1.3	0.9	1.4	0.8
7.5	0.5	0.5	0.7	0.6	1.3	0.8	1.8	1.1	2.6	1.3	2.8	1.4
15.0	0.7	0.7	1.0	0.8	1.6	1.0	2.5	1.4	3.2	1.7	3.5	1.6
22.5	0.8	0.8	1.2	1.0	2.0	1.2	2.8	1.7	3.7	1.9	3.8	2.0
30.0	1.0	1.0	1.3	1.1	2.0	1.3	3.2	1.9	3.8	2.0	4.1	2.1
37.5	1.1	1.0	1.5	1.1	2.5	1.5	3.5	2.0	4.0	2.0	4.3	2.2
45.0	1.1	1.0	1.6	1.2	2.6	1.5	3.7	2.1	4.0	2.1	4.3	2.4
52.5	1.2	1.1	1.6	1.3	2.8	1.6	4.0	2.1	4.3	2.2	4.6	2.4

The results obtained in varying the concentration of the chrome tanning solution and the temperature on the combination of the chromium complex from the new tanning solution, containing 0.06 *M* formic acid, are shown in Table V. The pH values of these solutions ranged from 3.94 to 3.09. The solutions gave no precipitation. The amount of chromium complex combined increased with each increase in temperature from 0° to 50° C. There is a reduced rate of increase in the chromium retention above 30° C. The take-up appears to reach a maximum at about 4 milliequivalents per gram of hide. Although the formic acid content of the tanning solution used in

*The amount of hide substance in the original squares was known, and the squares were weighed after tanning. Thus the ratio of Cr_2O_3 to hide substance could be calculated.

this experiment is the same as that used to obtain the results shown in Figure 1 and Table I, the chromium uptake is lower because the pH values are lower.

TABLE VI

INFLUENCE OF TEMPERATURE ON THE RETENTION OF CHROMIUM AND SULFATE BY THE HIDE SUBSTANCE OF CALFSKIN SQUARES TANNED IN SOLUTIONS CONTAINING VARYING AMOUNTS OF A CHROME TANNING AGENT AND NO FORMIC ACID.

Concentration of solution Meq. Cr_2O_3 or H_2SO_4 in 200 ml.	Meq. Cr_2O_3 or H_2SO_4 Retained by 1 g. Collagen											
	0°C.		10°C.		20°C.		30°C.		40°C.		50°C.	
	Cr_2O_3	H_2SO_4	Cr_2O_3	H_2SO_4	Cr_2O_3	H_2SO_4	Cr_2O_3	H_2SO_4	Cr_2O_3	H_2SO_4	Cr_2O_3	H_2SO_4
3.0	0.5	0.4	0.8	0.4	1.1	0.7	1.4	0.8	1.6	0.8	1.3	0.8
7.5	1.0	0.7	1.7	0.9	2.3	1.3	3.0	1.5	3.2	1.5	2.9	1.6
15.0	1.4	0.8	2.6	1.3	3.3	1.8	4.1	2.1	4.6	2.1	5.0	2.2
22.5	1.9	1.0	3.0	1.7	4.1	2.1	4.7	2.5	5.3	2.5	6.2	2.6
30.0	2.1	1.2	3.5	1.9	4.7	2.5	5.5	2.5	5.6	2.6	6.8	2.9
37.5	2.4	1.4	3.7	2.0	5.5	2.8	5.8	2.8	6.2	2.7	7.3	3.0
45.0	2.7	1.5	4.3	2.1	5.6	2.9	5.9	2.9	6.2	3.0	7.5	3.2
52.5	2.8	1.6	4.5	2.2	5.9	3.2	6.3	3.1	6.5	3.1	8.0	3.3

The retention of chromium complex by calfskin squares from solutions of the same concentrations as those for which results are given in Table V, but which contained no formic acid, is given in Table VI. The pH values of the solutions varied from 3.96 to 3.44. The results show an increase in take-up with increase in temperature. In the middle temperature range, 20° to 40°C., the increase in take-up with temperature is small, especially at the higher concentrations, compared with temperatures on both sides of this range. At 50° C. the maximum take-up is about 8 milliequivalents per gram; it appears probable that an appreciably larger chromium complex was formed at this temperature.

ANALYSIS OF THE RESULTS

By studying Tables V and VI it can be observed that the H_2SO_4 content appears to bear a relation to the Cr_2O_3 content as both increase with increase in temperature. Since it is known that hide combines with approximately equal amounts of H_2SO_4 at all temperatures, it appears that the increase in sulfate retention is associated with the composition of the combined chromium complex and that sulfate in some form is combined in the complex.

Considerable efforts have been directed toward the differentiation of protein-bound acid and the acid combined in the chromium complex. Gustavson (4) has shown that a part of the acid sulfate combined in chrome-tanned leather is more difficult to remove than the acid combined in pickled*

*Skins preserved in high concentrations of acid and salt, or treated with varying amounts of acid and salt before tanning.

skins. He found that all the acid was removed from pickled skins on neutralization to equilibrium at pH 5.5, while in the case of chrome leather a considerable amount of the original acid remained in the leather brought to equilibrium at the same pH. Gustavson (5) also found that the acid of pickled skin was completely removed by extraction with a 4% aqueous solution of pyridine. This was made the basis for a quantitative method for distinguishing between protein-bound acid and acid combined in the chromium complex. Merrill, Neidercorn, and Quarck (6), however, found that the pyridine displacement method did not give an exact separation between the two types of bound acid. They preferred the method originally proposed by Gustavson (4). This involves suspending the leather in water and adding sodium hydroxide solution in small increments for two days to maintain a constant pH of 5.4. Although considerable work was directed toward a separation of protein-bound acid and acid combined in the chromium complex, no highly satisfactory method was developed. Consequently, in the analysis of the results of this study, a different approach is tried for distinguishing between the two types of acid-binding in the leather.

Since the data in Tables V and VI suggest a relationship between chromium retention and sulfate retention, the values for the sulfate in milliequivalents H_2SO_4 per gram were plotted against the chromium in milliequivalents Cr_2O_3 per gram of hide. This plot is shown in Figure 3. All points fall close to a straight line except those for a few low Cr_2O_3 contents, at which equilibrium may not have been established in the leather. By the method of least squares the equation for the line in the figure was determined to be:

Milliequivalents H_2SO_4 = (0.41 x Milliequivalents Cr_2O_3) + 0.39. This is interpreted to mean that sulfate and chromium are combined in the leather

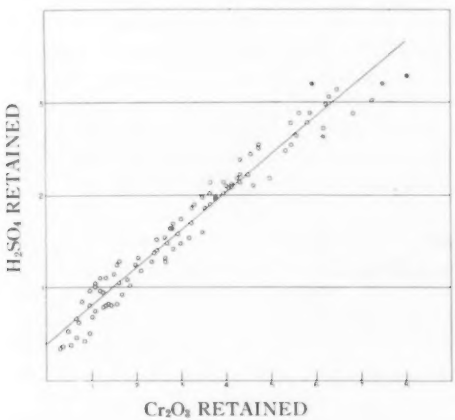


FIGURE 3.—Increase in the retention of sulfate expressed in milliequivalents of H_2SO_4 with increase in the retention of chromium expressed in milliequivalents of Cr_2O_3. The points include data for all temperatures.

in a definite ratio, and in addition a constant amount of sulfate is combined. This constant is the protein-bound acid, and in milliequivalents is almost exactly equivalent to the free amino groups of the lysine residues in collagen, which are the strongest acid-binding groups. The remainder of the sulfate is in the chromium complex where the ratio of H_2SO_4 to Cr_2O_3 is 0.41 to 1 or approximately 5 to 12.

The results shown in Figures 1 and 2 and Tables I, III, and IV indicate that the retention of chromium by hide increases with a rise in temperature and decreases with an increase in the amount of formic acid added. The formic acid probably acts in three ways to decrease the combination of the hide with chromium: (*a*) the hydrogen ions produced by the formic acid decrease the ionization of the carboxyl group in the protein: (*b*) the hydrogen ions, by decreasing the basicity of the chromium compounds, restrict hydrolysis to form large chromium complexes having tanning properties; and (*c*) it probably produces formato-chromium complexes which have lower affinity for collagen.

Although temperature increases the initial rate of the reaction of hide with chromium, the results in this work are not dependent upon the rates. No point is reached where the amount of chromium retained becomes constant; however, a period of 96 hours is sufficient for the reactions to reach a steady state; therefore, a shift in the equilibrium of the successive temperature reactions is involved. The rates do not influence the final results.

The apparent acidity* of the leather in per cent is plotted against milliequivalents of chromium, expressed as Cr_2O_3, in Figure 4. As the chromium

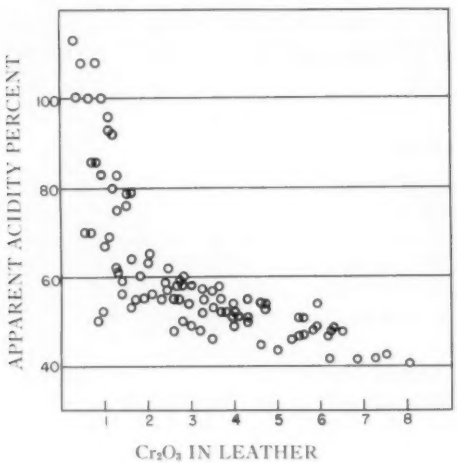
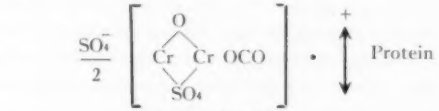


FIGURE 4.—Variation of the apparent acidity in percent with amount of chromium retained, expressed in milliequivalents of Cr_2O_3.

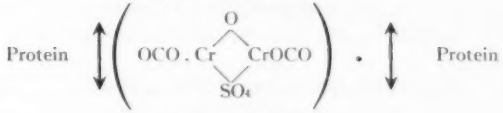
*Acidity is the ratio of sulfate in milliequivalents to chromium in milliequivalents expressed in percentage of the chromium.

content increases, the apparent acidity approaches 40% which, of course, agrees well with the ratio of one milliequivalent of chromium, expressed as Cr_2O_3, to 0.41 milliequivalent of H_2SO_4 found from the least squares calculation in Figure 3. It is interesting to note that Merrill and Schroeder (2) found almost identical results in their work on the influence of temperature on chrome tanning.

Cameron, McLaughlin, and Adams (7) have postulated that only the two-thirds basic salt of chromium acts as the tanning agent. The present results do not agree with this postulation, although a part of the chrome that combines is probably the two-thirds basic salt. A more probable type of chromium combining mechanism involves the unipoint- and multipoint-binding chromium complexes proposed by Gustavson (8). These two types of chrome complexes are given below.



Unipoint Binding



Multipoint Binding

The acidity of the unipoint complex is 50%, i. e., the ratio of chromium expressed as Cr_2O_3 to sulfate expressed as H_2SO_4 in milliequivalents is 6 to 3. In the multipoint complex the acidity is 33 ⅓ or a ratio of milliequivalents Cr_2O_3 to milliequivalents SO_4 of 6 to 2. The presence of equal amounts of these two types of chromium complexes in collagen would give the ratio 12 to 5 or an average acidity of about 41%.

Heats of combination of the chromium complex with hide were calculated by means of a generalized thermodynamic equation of the Vant Hoff type, assuming that the reaction between temperature intervals is reversible and that the heat of combination remains constant over a 10° range. Calculations of this type made over the range of 0° to 10° C. indicate that the heat of combination for 0.15 milliequivalents of chromium complex expressed as Cr_2O_3 is 10,900 calories per mol, for 0.2 milliequivalents 7500 calories per mol, and for 0.5 milliequivalents 2600 calories per mol. These results are similar to those of other reactions with collagen where the heats of combination are highest for the initially low concentrations of combining materials and decrease as these concentrations are increased.

The tanning reaction may be assumed to involve at least two separate reactions: (*a*) a hydrolysis to form the binding complex containing chromium

and sulfate, and (*b*) the actual combination with the active protein group. Reaction (*a*) involves the ionization of water and consequently is an endothermic reaction. Reaction (*b*) is probably an exothermic reaction since most reactions with the active group of collagen are of this type. The heat of the reaction is therefore the resultant of the two reactions; since this is positive or endothermic it appears that the hydrolysis may be the governing factor in the reaction.

Hydrolysis of the one-third basic chromium salt is required to produce a large active binding chromium complex. Assuming that the chromium complex combines with the carboxyl group, the total available carboxyl per gram of collagen is about 1.27 (9) millequivalents of which 0.2 to 0.3 milliequivalents is in the amide form in the limed hide; an even greater amount is in the amide form in the unlimed hide (10). Thus, the amount of carboxyl available is about 1 milliequivalent per gram. Complete saturation of these groups by unipoint combination would require 3 milliequivalents of chromium if the complex contained 1 chromium atom, or 6 if 2 chromium atoms were in the complex. Under only one set of conditions in these experiments did the chromium take-up amount to more than 6 milliequivalents per gram of collagen. Therefore, the combining chromium complex in these experiments, assuming 100% carboxyl participation, did not contain more than 2 to 3 chromium atoms.

It has been postulated that in order that the chromium complex be taken up by collagen, it is necessary that acid be removed from the solution by combination with collagen (7). Acid is a product of the hydrolysis which forms the chromium tanning complex, and in order for this reaction to continue, the acid must be removed from the solution. The results of this work, however, indicate that the amount of protein-bound acid combined reaches the same constant amount at all temperatures, whereas the amount of fixed chromium complex, containing acid and chromium in constant proportion,

TABLE VII

FINAL pH VALUES OF THE CHROME TANNING SOLUTIONS CONTAINING NO FORMIC ACID

Concentration of Chrome Tanning Solution Meq. Cr_2O_3 in 200 ml.	Final pH Values					
	0°C.	10°C.	20°C.	30°C.	40°C.	50°C.
3.0	3.90	3.96	3.77	3.71	3.70	3.70
7.5	3.79	3.82	3.64	3.55	3.56	3.46
15.0	3.68	3.69	3.58	3.53	3.52	3.46
22.5	3.63	3.63	3.52	3.51	3.51	3.45
30.0	3.61	3.59	3.51	3.51	3.50	3.44
37.5	3.60	3.57	3.49	3.48	3.50	3.44
45.0	3.58	3.54	3.48	3.48	3.50	3.44
52.5	3.57	3.52	3.47	3.47	3.49	3.44

increases with increase in temperature. The pH values of the tanning solutions, Table VII, decrease as the temperature is increased, indicating that apparently a different point of equilibrium is reached at each temperature and that it is not necessary that the collagen combine with all of the acid.

In order to form a large reactive chrome complex containing more than one chromium atom, hydrolysis of the chromium salt must occur. The type of hydrolysis that takes place to form a larger chrome tanning complex may be indicated by the following equation:

$$2\ CrOHSO_4 + 2H^+ + 2OH^- \rightleftharpoons \begin{matrix} OH & SO_4 & OH \\ \diagdown & \diagup & \diagdown \\ Cr & & Cr \\ \diagup & & \diagdown \\ OH & & OH \end{matrix} + H_2SO_4$$

This is a reversible reaction and if the amount of acid becomes sufficiently high the complex will decrease in size. Polychromium compounds containing more than two chromium atoms may be formed under suitable conditions.

The degree of ionization of water is well known to increase with an increase in temperature. Accordingly, more OH ions are available at a high temperature; therefore the hydrolysis should proceed more readily, and a larger complex should be formed.

PRACTICAL APPLICATION

In the dry-ashing of a chromium-tanned leather or a chrome-vegetable-retanned leather, the residue is chromic oxide and a small amount of neutral sulfate. Some of the constituents of the chromium complex are volatilized, and with the totals of the other constituents the analysis of the leather does not add up to 100% of the original weight. It is, therefore, impossible to obtain an accurate value for the amount of tannin which is determined by difference in a chrome-retanned leather. Some of the results obtained in this work are shown in Figure 5, in which 100 minus the percent hide substance is plotted against the content of chromic oxide. In leather tanned only with chromium, 100 minus the percent hide substance represents the weight of the chromium complex. Thus the plot is actually chromium complex against Cr_2O_3. By means of the least squares method the equation for this line was found to be

$$\text{Percent chromium complex} = (2.09 \times \%\ Cr_2O_3) + 2.78 \qquad \text{(I)}$$

Kubelka (12) has suggested that

$$\text{Percent chromium complex} = 2.73 \times \%\ Cr_2O_3 \qquad \text{(II)}$$

In Figure 5 his results are plotted as crosses, and those obtained in this work as circles. It may be noted that his data fit closely with the data obtained in

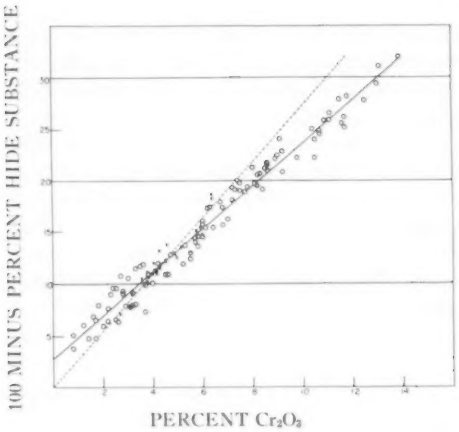


FIGURE 5.—Variation of the weight of the chromium complex (100 minus percent hide substance) with the percent Cr_2O_3 comparing Kubelka's values (X) with the results obtained in this work (O). Kubelka's factor.....; factor from results of this work ———.

this investigation. Kubelka's data, however, do not cover a large range of values, but for the range covered his equation fits quite well. Over a larger range of chromic oxide values equation (I) appears to be more applicable. With the use of this equation a more nearly correct value is obtained for the chromium complex, and consequently the tannin content may be determined more accurately by difference.

CONCLUSIONS

The following conclusions are based on the results obtained in the foregoing work:

1. Temperature greatly influences the amount of chromium complex combined in leather. These results agree with earlier work of Merrill and Schroeder (2).

2. An analysis of the data indicates that the protein-combined acid is a constant and is approximately equivalent to the free amino nitrogen of the amino acid lysine.

3. The ratio of the chromium (expressed as equivalents of Cr_2O_3) to sulfate combined with chromium (expressed as equivalents of H_2SO_4) is 12 to 5.

4. The apparent acidity in percent, i.e., ratio of chrome (Cr_2O_3) to sulfate (H_2SO_4), in the tanned leather is generally between 40 and 50% (more nearly 40%) which is in agreement with the work of Merrill and Schroeder (2).

5. The increase in the amount of chromium complex with increase in temperature is believed to be related to the increase in the ionization constant of water with increase in temperature. This promotes the hydrolysis and forms larger interacting chromium complexes.

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Received December 10, 1956.

DISCUSSION

DR. H. B. MERRILL (B. D. Eisendrath Memorial Laboratory): The data that Dr. Kanagy has presented have little direct application to practical chrome tanning for various obvious reasons, such as the fact that he used unpickled stock. Is that correct?

DR. KANAGY: Yes.

DR. MERRILL: The time was four days, and the ratio of chrome to collagen was in most cases much higher than is used in practice.

From a theoretical standpoint, this paper is of great interest, particularly in indicating that the basicity or acidity of the chrome complex that is fixed appears to be the same regardless of temperature, and that from the results obtained at different temperatures, one can calculate how much acid is fixed by the protein, as distinct from the amount combined with the chromium. That question of protein-bound versus chrome-bound acid has been discussed for the last 30 years, and various methods have been proposed to determine them separately, none of which is very satisfactory. I believe that this method of Kanagy's opens a new approach to that subject.

I would like to ask Dr. Kanagy whether he carried out any time studies. Were all your determinations made after 96 hours?

DR. KANAGY: That is correct.

DR. MERRILL: You did not get the rate of fixation at the different temperatures?

DR. KANAGY: No, I didn't get the rate. I obtained information from the literature that apparently equilibrium was reached in 72 to 96 hours. So I fixed the maximum time for my studies at 96 hours, and I did not make any rate studies.

DR. MERRILL: From a practical standpoint, the effect of temperature on the *rate* of fixation is, of course, more important than the effect of temperature on the ultimate amount fixed, because ordinarily a higher temperature is used to speed up the process rather than to increase the total amount fixed.

DR. THOMAS THORSTENSEN (Lowell Technological Institute): Dr. Kanagy, could you expand a little bit on the factor of pH in this particular study?

DR. KANAGY: I don't think the factor of pH had a great deal to do with the results. The results appear to fall on one straight line, even though there is a variation of pH. And if there were any great variation in pH, I know that that would have shown up.

Of course the highest pH always shows up in the most dilute solution. It is almost impossible to keep a constant pH for all the dilutions used.

DR. THORSTENSEN: The pH would be expected to vary considerably from one concentration to the next. Was there any correlation observed at a given concentration between pH and temperature?

DR. KANAGY: At the highest temperature we usually get the lowest pH. In other words, it appears that the more Cr_2O_3 is taken up, the more acid is formed in the solution. That is obvious because we started with a 33⅓% basic salt. The salt taken up by the protein is about 60% basic or 40% acidic, and that, of course, increases the amount of acid in the residual solution. That is why the fixation of the chrome is brought to an equilibrium and finally stopped.

DR. THORSTENSEN: Some years ago Dr. Theis and I did some work on the analysis of spent chrome liquors using exchange resins. We did not consider the data obtained to be accurate enough to warrant publication, but we did conclude that the chromium complex fixed had a more or less constant acidity.

The work you have shown us today is strong evidence in favor of a concept some of us have been considering for some time. I think you should be congratulated on this fine paper.

As early as 1300 A.D., Florentine tanners produced leather not only for footwear but also for books, saddlery, shields, wall hangings and upholstery.

—*Economics of Cattlehide Leather Tanning.* Merrill A. Watson, D.C.S. Chicago: The Rumpf Publishing Company, 1950.

LIFE LINES

Brief Biographies of Our Contributors

ALFRED W. HOPTON is a graduate of Cornell University. In 1933 he became associated with his father, the late A. W. Hoppenstedt, a charter member of this Association, in operating an analytical and consulting laboratory in Buffalo. Subsequently he worked for various chemical manufacturing companies and then opened his own research laboratory under the name of Niagara Industrial Laboratories, Niagara Falls, New York. Mr. Hopton joined ALCA in 1933.

DR. JOSEPH R. KANAGY was educated at Westminster College, Oberlin College, and the University of Maryland. He received his Ph.D. from the last-named institution. He has been on the staff of the National Bureau of Standards for some 27 years, and currently is Chief of the Leather Section. He became an active member of the Association in 1943, has served the Association as a member of the Council, and has been active in several committee assignments. His numerous and valuable papers, many of which were published in this Journal, were fittingly recognized by the Alsop Award in 1952.

Victor Mattei did his undergraduate work at Xavier University, Cincinnati, Ohio and received his M.S. from the same institution in 1952. His major field of study was organic chemistry. He has been a research associate in the Tanners' Council Laboratory at the University of Cincinnati since 1952, working chiefly on fatliquoring of leather.

WILLIAM T. RODDY, a graduate of the University of Cincinnati, has been associated with the Tanners' Council Research Laboratory at the University for over 25 years. He joined ALCA in 1939 and has served on the Physical Testing Committee, Preparatory and Post-Tanning Processes Committee, and the Council. His numerous publications, chiefly in this Journal, have contributed much to our knowledge of the structure of skin, beamhouse processes, tanning, and posttanning operations.

With the development of the chrome process for upper leather and the growing supplies of hides in the Middle West in the post-Civil War period, Chicago developed a number of large tanneries in the vicinity of packing houses. Milwaukee, not far away, became one of the most important tanning centers in the country. During the period 1880-1890, large numbers of sole leather tanners established themselves in Virginia, Tennessee, and other southern states.

—*Economics of Cattlehide Leather Tanning.* Merrill A. Watson, D.C.S. Chicago: The Rumpf Publishing Company, 1950.

ALCA NEWS

Proceedings, Reports, Notices, and News

of the

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PROF. F. O. SCHMITT HONORED

Francis O. Schmitt, Professor of Biology at Massachusetts Institute of Technology, shared in a recent Albert Lasker Award for "pioneering studies of the biochemical components of connective tissues." Professor Schmitt, an active member of ALCA, has published several papers on the structure of collagen, as revealed by electron micrography, in this Journal.

SECRETARY'S NOTICE

Any member or person who may wish to present a paper at the International Union of Leather Chemists Societies Meeting in Rome, Italy, on September 15–19, 1957, please advise the ALCA Secretary by May 1, 1957.

Dr. Fred O'Flaherty
Secretary

NECROLOGY

The deaths of the following members of the Association are announced with deep regret:

William Z. Beier, an associate member since 1934, died on November 30, 1956. After graduating from Pratt Institute, Mr. Beier was employed successively by G. F. Zeller's Sons and the Cataract Chemical Company. In 1935 he helped found the Buffalo Extract and Supply Company, of which he became sole owner in 1946.

August Boss, an active member since 1937, died on December 5, 1956. Previously affiliated with A. C. Lawrence Leather Company, Beebe Tannery, Burk Brothers, and Hartland Tanning Company, at the time of his death he was Vice President in charge of upper leather production for Howes Leather Company.

Louis Erera, an active member since 1943, died on October 16, 1956, aged 41. He had been Assistant Superintendent of the Specialty - Newcastle Division, Allied Kid Company.

Ellis B. Miller, an associate member since 1948, died on December 3, 1956, aged 39. At the time of his death he was employed as a sales representative by the Newark Leather Finish Company, Harrison, New Jersey.

FIFTY-THIRD ANNUAL MEETING

PRELIMINARY ANNOUNCEMENT

The Association will convene for its Fifty-third Annual Meeting, June 2–5, 1957, at the Lake Placid Club, Essex County, New York. The site selected appears to offer everything that can be desired for the annual assembly. The Club is situated in one of the beauty spots of America, in the heart of the Adirondacks, on beautiful Mirror Lake, 1864 feet above sea level. The man-made facilities are almost as imposing as the scenery. They include an auditorium seating 850 people, two 18-hole golf courses and one 9-hole one, twelve tennis courts, and facilities for swimming, boating, riding, skeet, outdoor shuffleboard, squash, badminton, ping-pong, pool, and billiards. There are also a 10,000-volume library, a chapel, and a medical unit staffed by a physician, dentist, and registered nurse.

The Club can be reached by New York Central Railway, which runs an overnight sleeper from New York, via Utica, arriving at 8:15 A.M. The returning train leaves Lake Placid at 8:35 P.M. Arrangements can be made for through sleeping cars from Chicago, to be connected at Utica. Eastern Airlines provides planes from New York City to Lake Clear Airport, 15 miles from the Club. The Club provides transportation from the airport. Driving distances are: 317 miles from New York, 307 from Boston, 877 from Chicago, and 347 from Toronto.

The Convention Committee consists of: *Chairman*, Clinton R. Retzsch; *Vice-Chairman*, Robert Stubbings; *Hotel and Transportation*, Harold Bernard; *Publicity*, Joseph J. Stellmach; *Golf*, William Hammel and Marden I. Lindsay; *Entertainment*, Joseph A. Casnocha and Fred Klimpl; *Ladies' Activities*, Mrs. Harold Bernard.

Further announcements concerning the program will be published in later issues.

ALCA - ASTM JOINT COMMITTEE ON LEATHER

SYNOPSIS OF MINUTES OF MEETING OCTOBER 22, 1956

Each subcommittee and section met separately, after which the main committee met to hear reports from the subcommittee and section chairmen. The reports follow:

SUBCOMMITTEE NO. 1—NOMENCLATURE AND DEFINITIONS

R. M. Lollar, *Chairman*

Section 5 of Federal Specification KK-L-311a will be used as the primary source of definitions of leather terms. An amended list of terms, restricted

at present to terms encountered in the evaluation of physical properties, will be prepared for ballot within the subcommittee and eventual presentation to the Joint Committee. All methods should be submitted to this subcommittee for approval of the sections on scope and definitions before they are submitted to the Joint Committee.

SUBCOMMITTEE NO. 2—SAMPLING AND CONDITIONS FOR PHYSICAL TESTS

C. W. Mann, *Chairman*

The sampling plans contained in Federal Specifications will be adopted wherever possible. New sampling plans will be written to cover leathers for which there is no Federal Specification sampling plan at present.

SUBCOMMITTEE NO. 3—GENERAL PHYSICAL TESTING

George Butz, *Chairman*

Section No. 2—Physical Dimensions.—J. Naghski, *Chairman*

The 5 applicable ALCA methods (E2, E3, E4, E5, and E45) will be rewritten in the proper form and submitted to ballot.

Section No. 3—Tensile Properties.—R. Young, *Chairman*

Method E15 (Tensile Strength) will be considered first, followed by Methods E13, E16, and E17. Each method will be rewritten and submitted to ballot.

Section No. 4—Effect of Water.—R. Ashcraft, *Chairman*

This committee proposes to accumulate and study all known methods for testing water resistance and water repellency of shoe upper, sole, glove, garment, upholstery, and mechanical leathers. The committee will establish a sampling plan, obtain samples, test them, and correlate the results with actual performance tests in the evaluation of each method that will be studied.

Section No. 5—Surface Characteristics.—R. Stubbings, *Chairman*
(replacing L. D. Compton, resigned)

Plans have been made to divide the work among working groups, and to study ALCA Methods E42 (Cold Failure), E 44 (Staining), and E 46 (Bleeding and Crocking); also water spotting, fading, scuff resistance, flex, and adhesion.

Section No. 6—Fire Resistance.—R. Stubbings, *Chairman*

This committee proposes to study flame resistance only, but asks whether it should also consider other thermal effects.

Section No. 7—Mechanical Leathers (Miscellaneous Properties).—A. N. Compton, *Chairman*

A method for making a corrosion test, based on Specification MIL-R-5521A, has been rewritten, approved by letter ballot within the section, approved by Subcommittee No. 1, and is being considered by the Editorial Subcommittee. A method for determining the porosity of leather packings, which has been approved by the National Industrial Leather Association, is being reviewed.

Section No. 8—Deterioration Effects.—S. S. Kremen, *Chairman*

This committee is concerning itself initially with a method for determining perspiration resistance. The first problem is to decide upon, and evaluate, a proper solution of reagents.

Section No. 9—Bond Strength of Belting Leather.
P. Rhoads, *Chairman*

Specification KK-B-201C will be used as the basis for a method under consideration by this committee.

Section No. 10—Miscellaneous Physical Properties.
A. N. Kay, *Chairman*

ALCA Method E43 (Stiffness) will be rewritten for consideration.

SUBCOMMITTEE NO. 4—RESEARCH

M. M. Baldwin, *Chairman*

The scope of this subcommittee's activities was discussed, and the following points were suggested for consideration by the Advisory Committee: (1) Compile a list of current research on test methods, to include investigations undertaken by the subcommittees and sections of the ALCA - ASTM Joint Committee and by the leather industry in general. **See notice below.** (2) Make recommendations as to areas of research on new test methods. (3) Act on problems assigned or authorized by the Advisory Committee. (4) Arrange for presentation of papers on research on testing methods in technical programs at meetings of the ALCA - ASTM Joint Committee.

SUBCOMMITTEE NO. 5—EDITORIAL

L. Boor, *Chairman*

The scope of this committee has been considered.

The next meeting of the Joint Committee is scheduled to be held in New York, during the second week in February, at a date to be announced later.

M. H. Battles, *Secretary*

NOTICE

Dr. M. M. Baldwin, Battelle Memorial Institute, Columbus, Ohio, would appreciate hearing from any reader of this Journal knowing of a new method of test for leather. At present his interest is restricted to physical tests, but in the future he will be concerned with chemical tests also.

CORRESPONDENCE

The following correspondence has been received by the editor:

Dear Sir,

In the November, 1956, issue of JALCA on page 605 is the amazing statement that oil tannage of buckskin originated in the USA, and it was in the year 1810. The *facts* are that oil tannage is a very old process: tanners of "buffe and shamoys" are mentioned in the charter of King James 1st granted to the "Wardens and Mistery of Leathersellers of London" in 1604. I feel sure that if time were available, references much earlier than this could be found.

Mr. Joseph Nathan Kane should be more careful of his claims.

Yours faithfully,

S. E. F.
Information Officer
The British Leather Manufacturer's
Research Association
Milton Park, Egham, Surrey, England

The Information Officer is right, of course. Oil tannage is very old indeed and was undoubtedly practised many centuries before King James's time. Mr. Kane's statement probably refers to the first commercial production of oil-tanned leathers in the United States.—EDITOR.

CHEMIST WANTED

ORGANIC CHEMIST wanted with good theoretical knowledge and laboratory experience, for research and development work. Tanning experience desirable but no condition. Reply to Box 218FA, c/o Dr. Fred O'Flaherty, Secretary, American Leather Chemists Association, University of Cincinnati, Cincinnati 21, Ohio.

ABSTRACTS

Sedimentation Studies of Epidermal Keratins. Keratin A and Keratin B. A. G. Matoltsy. *J. Biophys. Biochem. Cytol.*, **2,** 361–63 (1956); *Chem.*

The Structure of Collagen Molecules and Fibrils. R. S. Bear. *J. Biophys. Biochem. Cytol.*, **2,** 363–68 (1956); *Chem. Abstr.*, **50,** 15639*c*.

Further Observations on the Transformation of Collagen Fibrils into "Elastin", and Electron Microscope Study. M. K. Keech, R. Reed, and M. J. Wood. *J. Pathol Bacteriol.*, **71,** 477–93 (1956); *Chem. Abstr.*, **50,** 15640*f*.

Tanning Extracts from Spruce Cones. A. Suszer, G. Alexandrescu, and G. Ganea. *Rev. Chim.* (Bucharest), **6,** 465–66 (1955); *Chem. Abstr.*, **50,** 16147*i*.

Synthetic Tanning Agents from Wood Phenols. D. Tishchenko and I. P. Uvarov. *Gidroliz. i Lesokhim. Prom.*, **9,** No. 2, 9–11 (1956); *Chem. Abstr.*, **50,** 16149*a*.

Italian Leather Research. Anon. *Leather World*, **48,** No. 35, 9 (1956). —The Naples Research Laboratory for the Tanning Industry, with Prof. Simoncini as Director, will embark on a program to (1) study beechwood extract as a tanning agent; (2) compare the tanning values of wattle and chestnut wood extracts; (3) establish a rapid method of determining the bacteriostatic power of antiseptics; (4) determine the modulus of elasticity characteristics of heavy leather; (5) determine whether the use of silicones in leather affects characteristics other than water repellency; and (6) collect, determine tolerance limits of, and publish methods of physical testing for the technical control of leather. J.J.

Investigations on Bating. II. The Laboratory Evaluation of Bating Activity. G. H. Green. *J. Soc. Leather Trades' Chemists*, **40,** 361–77 (1956).—Experimental bating trials were conducted with gelatin as a substrate. A gelatin viscosity reduction method was employed for determination of enzyme proteolytic activity. A unit of gelatinase activity was defined in terms of the rate of increase in fluidity of a gelatin solution at a stated pH and temperature. The viscosity of the gelatin substrate decreased continuously on storage at 20°C. but remained constant at 0°–4°C. However, even after two months at 20° the apparent activity of trypsin toward the substrate remained the same. Electrolytes lowered the substrate viscosity but did not affect the determination except when the enzymes were inhibited. Ammonium salts at a bate paddle concentration severely inhibited *Bacillus subtilis protease*. Excellent correlation was obtained between gelatinase activity and bating activity as assessed by laboratory bating and chrome tannage of pieces of goatskins

treated with a wide variety of enzymes. The gelatin viscosity method is recommended for evaluation of bating materials. A quantitative procedure for assaying the activity of proteolytic enzymes toward digestion of involuntary muscle is described. There was no correlation between involuntary muscle-digesting activity and bating activity. J.M.C.

The Utilization of Organo-silicic Polymers in Improving the Hydrophobic Nature of Tanned Skins. A. Ionescu. *Rev. Chim.* (Bucharest), **6,** 591–93 (1955); *Chem. Abstr.*, **50,** 17506*e*.

Synthetic Leather Oils and Fats. B. M. Das, D. Ramaswamy, and Y. Nayudamma. *Indian Soap J.*, **20,** 71–80 (1954); *Chem. Abstr.*, **50,** 17506*f*.

New Apparatus for Testing Freeze Resistance of Artificial Leathers. O. Ordelt. *Chem. Prumysl*, **6,** 240–43 (1956); *Chem. Abstr.*, **50,** 17507*g*.

Effect of Aureomycin, Nitrite, and Ricinoleate on Red Halophylic Bacteria. R. Venkataraman and A. Sreenivasan. *Current Sci.* (India), **25,** 190–91 (1956); *Chem. Abstr.*, **50,** 16969*a*.

The Structure of Gelatin. Effect of the Molecular Mass on the Rigidity of Gels. J. Pouradier, A. M. Venet, and L. Trigny. *Compt. Rend. 27th Congr. Chim. Ind.*, 769–71 (1954); *Chem. Abstr.*, **50,** 16278*e*.

Oil Tanning. I.—H. Nozaki and H. Hamada. *Bull. Natl. Inst. Agr. Sci.* (Japan), Ser. G, No. **4,** 41–45 (1952). **II.**—H. Nozaki, H. Hamada, and I. Fujinuma. *Ibid.*, No. **6,** 103–10 (1953); *Chem. Abstr.*, **50,** 17503*d*.

The Reaction of the Salts of Trivalent Chromium with Glycine and with Alanine. L. M. Volshtein. *Izvest. Sektora Platiny i Drug. Blagorod. Metal*, **27,** 20–32 (1952). **The Action of Acids on the Internal Complex Compounds of Trivalent Chromium with Glycine and Alanine.** *Ibid.*, **27,** 33–46 (1952). **Electrical Conductivity of the Glycine Complexes of Chromium.** L. M. Volshtein and A. P. Bavrin. *Ibid.*, **27,** 47–61 (1952); *Chem. Abstr.*, **50,** 16515*c–f*.

Electrochromatography. XIV. Separation of Hydration Isomers of Chromic Chloride and Chromic Sulfate. M. Maki. *Japan. Analyst*, **4,** 547–49 (1955); *Chem. Abstr.*, **50,** 16530*c*.

Comparative Examinations of Crystalline Procollagen from Various Kinds of Animals. I. Komjat and F. Antoni. *Acta Physiol. Acad. Sci. Hung.*, **9,** 339–50 (1956) (in German); *Chem. Abstr.*, **50,** 16890*a*.

Structure of Collagen and Its Species Peculiarities. A. L. Zaides. *Biofizika*, **1,** 279–83 (1956); *Chem. Abstr.*, **50,** 16901*c*.

Wool Grease. T. Miyakawa. *Repts. Osaka Ind. Research Inst.*, No. 304, 116 pp. (1955); *Chem. Abstr.*, **50,** 17477*c*.

The Chrome Solution for Tanning. H. Nozaki and H. Hamada. *Bull. Natl. Inst. Agr. Sci.* (Japan), Ser. G, No. **4,** 47–52 (1952) (English summary); *Chem. Abstr.*, **50,** 17501*e*.

Determination of the Molecular Size of Colloidal Chromium Complexes with Ion Exchanger. II. A. Kawamura and H. Okamura. *Bull. Japan Assoc. Leather Technol.*, **1,** 95–105 (1956); *Chem. Abstr.*, **50,** 17501*i*.

X-Ray Diffraction Studies of Collagen Fibres. P. M. Cowan, A. C. T. North, and J. T. Randall. *Symposia Soc. Exptl. Biol., No. 9, 1954, "Fibrous Proteins and Their Biol. Significance"*, 115–26 (1955).—High- and low-angle X-ray diffraction by collagen fibers is discussed. When a collagen fiber is extended by loading, the low-angle spacing (640 A) varies directly with the fiber length. The variation is not due to slip, because points for both extension and relaxation fall on the same line. The high-angle spacing (2.86 A) also varies, but proportionately much less than the low-angle spacing. Stretching the fiber sufficiently to cause a 10% increase in the low-angle spacing causes an increase of only 4.3% in the high-angle spacing. These results indicate the probable existence of two types of regions, differing in their degree of order. The variation in intensity of the orders of the large period suggests that the diffracting unit is spherical or ellipsoidal with length 210–240 A in the fiber direction. Still smaller subunits 70–80 A long may also exist. Calculation from the low-angle X-ray scattering also gives about 200 A as the dimension in the fiber direction, and from 40 to 90 A, depending upon the moisture content, at right angles. Rat tail tendons that have not been allowed to dry give X-ray patterns indicative of large-scale lateral order not observed in dry or rewetted fibers. It is evident that the moisture present naturally in collagen contributes to a much higher degree of lateral order than has been supposed, and that much of this order is irreversibly lost on drying. The structural model requirements for the collagen protofibril, arising from the high-angle X-ray diagram of stretched collagen fibers, are discussed, and various approaches to the development of such models are indicated. J.H.H.

Observations on Native and Precipitated Collagen. J. T. Randall, F. Booth, R. E. Burge, S. F. Jackson, and F. C. Kelly. *Symposia Soc. Exptl. Biol., No. 9, 1954, "Fibrous Proteins and Their Biol. Significance,"* 127–47 (1955).—Densitometer traces were made of the band structure in electronmicrographs of unstained, unshadowed collagen fibrils from rat tail tendon and fowl neck tendon. Differences between the two materials are small. The results are used to calculate the longitudinal variation of fibril density from which in turn the low-angle X-ray diffraction pattern may be calculated. The factors involved in the precipitation of collagen fibrils from solution are discussed, and experimental results are given which show that the largest single factor is change of pH. This means that the electric charge and its distribution on the molecule are the primary factors in the precipitation. A theoretical analysis is given of the coagulation of thin, uniformly charged rod-shaped particles.

This leads to the conclusion that for such a model there is no strong preference for fibrous precipitation rather than a random gel. In the actual case of collagen, however, the alternation of charges of both signs would provide additional short-range attractions. The conditions under which the complex forms, fibrous long spacing (FLS) and segment long spacing (SLS), are produced and interconverted with each other and with collagen are discussed. Densitometer tracings are given of the fine structure of FLS and SLS. FLS varies far more in structure, with the method of formation, than does SLS. In contrast to normal fibrous collagen, which is probably formed from a single protein constituent, FLS and SLS are possibly formed by the association of a soluble collagen fraction with another molecule, usually, but not always, macromolecular. J.H.H.

Configuration of Collagen and Gelatin Molecules in Condensed and Dispersed States. R. S. Bear. *Symposia Soc. Exptl. Biol., No. 9, 1954, "Fibrous Proteins and Their Biol. Significance,"* 97–114 (1955).—The wide-angle X-ray diffraction by collagen and its interpretation in terms of helical models proposed prior to 1955 are reviewed. The relation to this subject of work on protofibrillar dispersions of collagen and on the reconstitution of various fibrous forms from solution is also discussed. J.H.H.

The Chemistry of Keratinous Structures. J. B. Speakman. *Symposia Soc. Exptl. Biol., No. 9, 1954, "Fibrous Proteins and Their Biol. Significance,"* 169–82 (1955).—A review of recent work (largely on wool) on the constitution, accessibility of the structure to various reagents, and reactivity of the disulfide bond. J.H.H.

States of Aggregation of Collagen. F. O. Schmitt, J. Gross, and J. H. Highberger. *Symposia Soc. Exptl. Biol., No. 9, 1954, "Fibrous Proteins and Their Biol. Significance,"* 148–62 (1955).—Highly purified collagen from cowhide contains about 0.4% tyrosine, 0.4% hexose, mainly as galactose and glucose, and a trace (0.05%) of hexosamine. Such material shows no enhanced solubility in acid, and it seems improbable that the trace of mucopolysaccharide that could be present could play any significant role in the stabilization of the structure. The authors' previous work on the structure, composition, and modes of formation of fibrous long spacing (FLS), segment long spacing (SLS), and collagen, and on the interconversion of these forms, is reviewed. This work led to the conclusion that these various forms are produced by different modes of aggregation of a single kinetic unit, which it is proposed be denoted by the term "tropocollagen". The tropocollagen particle is about 2000 A in length and very thin, being composed of only a few polypeptide chains. This unit is assumed to be the biological precursor of collagen. The various modes of aggregation by which collagen, FLS, and SLS are formed from tropocollagen are discussed. J.H.H.

Comparison of Lime Solutions Made from CaO and $Ca(OH)_2$. E. Gratacos Masanella, *Bol. Asoc. quim. espanola*, **44**, 228–33 (1956).—Two lime solutions were prepared containing (A) 5% CaO and (B) 6.6% $Ca(OH)_2$ (the latter in powder form). One sheepskin, previously soaked, dehaired, and

lightly fleshed, was cropped and then divided into 12 equal pieces. Six pieces each were put in lime A and 6 in lime B, always entirely covered. Every 4 weeks the lime bath was refreshed. After 15, 30, 60, and 90 days a piece was removed, air-dried, and analyzed for amide nitrogen. A corresponding piece was delimed, bated, chrome-tanned, neutralized, fatliquored, and dried. The analytical results indicate that the degradation of collagen is higher in lime A with a slow sedimentation rate than in lime B with a fast sedimentation rate. Collagen without lime treatment contains 6.13 mg. of amide nitrogen per g. collagen. For changes occurring in the two lime solutions, see the following table:

Days in lime	Mg. amide N/g. collagen after lime	Mg. amide N degraded/collagen
15 (A)	5.10	1.03
15 (B)	5.51	0.62
30 (A)	3.45	2.68
30 (B)	4.57	1.56
60 (A)	2.46	3.49
60 (B)	3.87	2.26
90 (A)	1.77	4.36
90 (B)	2.73	3.40

The finished leather out of lime A (60 days) showed very tender grain and was bone-hard; out of lime B the leather was softer and showed unmarked grain. However this effect on the leather is only true for still liming. Where drums or paddle vats are used there is no difference in the finished leather.

H.K.

Use and Abuse of pH Measurements. I. Feldman. *Anal. Chem.*, **28,** 1859 (1956).—The development of the concept of pH from its invention by Sorenson in 1909 to the present-day National Bureau of Standards' pH scale is reviewed. The liquid junction potential problem involved in the use of the pH meter is discussed in detail. The magnitude of the error due to the junction potential depends upon the pH, ionic strength, nature of the solutes, nature of the solvent, presence of colloids, and temperature—in fact, anything that affects the mobilities of charged particles. Whether the junction potential error can be ignored depends upon the use to which the pH measurement is put. Some estimates from the literature as to the probable magnitude of this error are presented and discussed. Under certain relatively simple conditions an approximate relationship may be considered to exist between the pH meter reading and the hydrogen ion concentration. Under other conditions the pH meter reading must be considered as simply a reproducible reference point having no theoretical significance. Under some conditions the meter reading cannot even be considered as a reproducible reference point. These points are developed in detail. Author's abstract

BOOK REVIEW

The Chemistry and Technology of Leather. Vol. I. Preparation for Tannage, ed. F. O'Flaherty, W. T. Roddy, and R. M. Lollar. A. C. S. Monograph No. 134. New York: Reinhold Publishing Corporation, 1956. 495 pp. $14.—This is an ambitious and largely successful attempt to cover the practice of this phase of leather making as well as the scientific aspects. Edited by Fred O'Flaherty, William T. Roddy, and Robert M. Lollar of the Tanners' Council Research Laboratory, it helps to fill the need of an advanced text book.

Since each one is written by a different specialist, it seems desirable to say something, however brief and inadequate, about each chapter.

Dr. O'Flaherty has been almost too considerate of our time in writing an introductory chapter of only three pages. The idea that organic solvent tannages will become a popular practice in the relatively near future seems somewhat optimistic to this reviewer.

In Chapter 2, after covering the fundamentals of the Histology of Animal Skins, William T. Roddy goes on to discuss skin and hide defects, structural changes during processing, tannery damages, and the relationship of structure to the properties of the leather, all of which is useful to the tanner and chemist.

In Chapter 3 Robert M. Koppenhoefer gives a review of the Non-Protein Constituents of the Skin. Dr. Koppenhoefer's research on the lipides of the skin is well known and has added substantially to our knowledge of their nature and distribution.

Chapter 4 on The Chemical Structure and Macromolecular Organization of the Skin Proteins is written by the recent Alsop Award winner, John H. Highberger. Knowledge in this field is expanding at a phenomenal rate. Recent discoveries about the structure of collagen, in which Dr. Highberger is participating, have a profound bearing on biochemistry and medicine, as well as broad significance to the leather industry. This continuing research deserves the attention of tanners for its practical implications for the future.

F. L. DeBeukelaer, author of Chapter 5, is an authority on the Preservation of Hides and Skins. The discussion of salting and brine-curing, the latter as practiced in the United States and Argentina, brings out the different procedures clearly.

Arthur W. Goetz does Chapter 6 on Washing and Soaking. It is apparent that bacterial damage in the soaks, which received so much attention in the past, is no longer a serious problem. The inability of conventional wetting agents to accelerate soaking might have been mentioned.

Wendell Morris, in Chapter 7 on The Practice of Unhairing, emphasizes that the simultaneous effects of liming on the skin are at least as important as the unhairing itself. The limitations of the hair-pulping method are brought out. The first formula in the section on goatskins is somewhat misleading, since goatskins are commonly unhaired in one liquor in three to five days. Imported sheepskins such as Cabrettas and Sudans for fine glove leather should be referred to as hair sheep, rather than wool sheep.

Chapter 8 on The Mechanism of Unhairing is by Henry B. Merrill. As one of the pioneers in the reduction theory of unhairing, he gives an authoritative review of widely scattered literature. Dr. Merrill points out that Atkin and Thompson, writing in the *Leather Trades Year Book* in 1926, were the

first to suggest that the sulfide reduces the cystine of the hair to cysteine, thereby permitting unhairing. This reference has been overlooked by many workers in this field. Dr. Merrill's conclusions appeal to this reviewer as clear and accurate.

Chapter 9, The Chemistry of Liming, is by Robert M. Lollar. This subject is a difficult research field because there are no convenient analytical methods for measuring moderate chemical changes in an insoluble protein. This reviewer feels that there is still no wholly adequate correlation in the literature of the practical or chemical relationships between different liming systems from completely mellow to strongly sharpened. Such factors as the amount of swelling of the collagen and the length of time in the liquor have an important bearing on the quality of the finished leather.

Harry R. Wilson takes up The Practice of Bating in Chapter 10. In an operation involving many procedures and using a combination of a neutralizing agent and a mixed organic catalyst of unknown protein structure and undefined strength, it is not surprising that some aspects are still a matter of opinion. The inclusion of an acid wash in the procedures given for bating calf and side leather may imply more than is intended. This is qualified in a later section about the acid wash. The drastic bating of glove leather is primarily to influence the properties of the finished leather, such as "run". Scud could be removed by a lighter bating. It might have been mentioned that an interesting change in the kid industry has taken place in fairly recent years from old puers to fresh bates, even for glazed kid.

Julius Pfannmuller, in Chapter 11, entitled Bating, writes an impartial survey covering the different enzymes in bates and the tissues upon which they act. It would seem that more questionable theories have been postulated about what takes place in bating than about any other single step in leather making. The voluminous literature has been reviewed and evaluated in the light of present knowledge and Dr. Pfannmuller's extensive personal experience.

Textile authorities Robert Saxon and Milton Harris collaborate in Chapter 12 on The Acid and Base Binding Properties of Proteins. The section on collagen serves to emphasize the importance of the relatively high content of acidic and basic side chains in leather chemistry, as in the operations of pickling, tanning, and dyeing.

Robert Stubbings, in Chapter 13 on Pickling, uses the ingenious method of an industry-wide questionnaire which gives an interesting cross-section picture of commercial practice. Dr. Stubbings wisely cautions that the present trend to a more rapid pickle-tan cycle requires more careful attention than does the equilibrium pickling process. A second section covers the chemistry of pickling.

Kenneth G. A. Pankhurst of the British Leather Manufacturers' Research Association contributes the last chapter, entitled Skin Degreasing. Dr. Pankhurst discusses the three methods of degreasing, two of which we are likely to overlook because of the predominence of the third. The influence of synthetic emulsifiers is carefully explained and is particularly helpful, since there is little literature on this subject. The brine washing which is regarded as important in American practice is covered rather briefly.

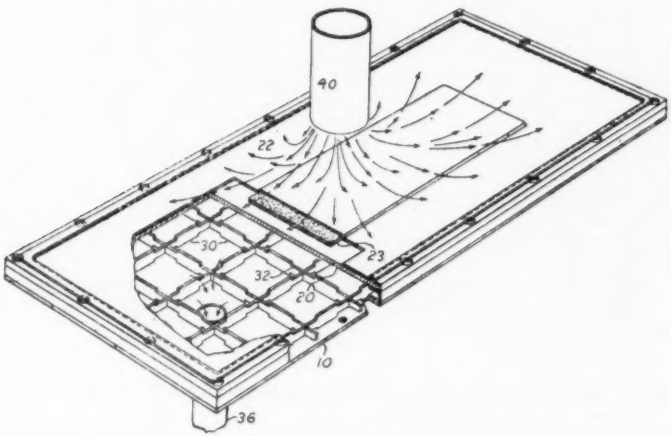
Leather literature helps to supply the knowledge that is indispensable to cope with the many problems which arise today. *The Chemistry and Technology of Leather* is a substantial aid in this respect, and we can look forward to further assistance from the three succeeding volumes. This work will be particularly

helpful to those of us who are not able to keep up with the original literature. This monograph should be in the library of every leather chemist.

Wallace Windus

PATENTS

Drying Leather. Brit. Pat. 750,416. British United Shoe Machinery Co., Ltd. (United Shoe Machinery Corporation). Apl. June 8, 1954.



Hides or skins are dried by confining the workpiece between the surfaces of a plane rigid member and a flexible member, one of which is vapour transmissive when wet, and applying heat and vacuum to the workpiece so confined in such a manner as to cause the flexible member to press the workpiece against the rigid member. Preferably the workpiece is confined between the surfaces of a porous plate and a flexible impermeable sheet, heat applied to the workpiece thus confined and the vacuum applied to the surface of the porous plate opposite that with which the workpiece is in contact. In the illustrated apparatus the leather to be dried, 23, is supported on a plate 20 made of porous material and covered by a flexible sheet 22 which extends over the leather and contacts the porous plate 20 beyond the periphery of the leather. The plate 20 is spaced from a supporting face plate 10 by a series of cross-pieces 30 provided with inter-connecting channels 32 and a vacuum is applied to the space below the plate 20 by a vent 36 connected to a pump. A duct 40 supplies hot air to the upper surface of the impermeable flexible sheet 22. Alternatively heating may be effected by infra-red lamps. Shrinking of the workpiece during drying is prevented by the action of the flexible sheet which holds the workpiece firmly against the porous plate 20. The grain surface of the workpiece is in contact with the impermeable sheet 22. The porous plate 20

may be made of sintered ceramic or metal or of a heavy wire mesh or other rigid perforated surface covered with felt, its essential characteristic being that it is vapour transmissive when wet.

Artificial Leather; Agglutinated Fibrous. Brit. Pat. 751,017. Du Pont de Nemours & Co., E. I. Apl. Dec. 10, 1953.—A water vapour-permeable leather substitute is made by hot-pressing a sheet consisting of fibres and a thermoplastic polymeric binder having a lower softening point than the fibres, soaking the resulting substantially impermeable sheet in a liquid which swells the fibres, at a temperature above the softening temperature of the polymeric binder, and finally cooling the sheet and drying to remove the liquid. The fibres, which may constitute 20–70% of the volume of the sheet, are preferably at least 0.5 inch in length, and may comprise cotton, wool, viscose or acetate rayon, polyamides such as nylon, polyethylene terephthalate, acrylonitrile polymers or copolymers, or polyvinyl acetal. The polymeric binders used are those referred to in Specification 737,137. The binder may be introduced (a) as a homogeneous film which is pressed into a carded web of the fibres, (b) as fibres which may be made into a carded web or a paper with the other fibres, (c) as an aqueous dispersion which is formed into a mixed dispersion with the fibres, or used to impregnate a fibrous mat, (d) as a solution which is used to impregnate a fibrous mat, (e) as a powder, or (f) as a calendered coating. The liquid used to soak the sheet may be water, which may contain sodium chloride or acetate in solution. The quantity of binder may vary from one surface to the other, and the product may be embossed during the hot-pressing operation. Specifications 461,236 and 535,262, [*both in Group* IV], also are referred to.

Leather Replacement Compositions and Process. U. S. Pat. 2,772,995. J. D. C. Wilson, II, New Castle, Del., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware. Apl. May 7, 1954.—1. The process of forming non-woven, porous leather replacement fabrics which comprises associating substantially water vapor-impermeable, relatively extensible, initially thermoplastic, elastomeric, polymeric binder material with a fibrous sheet comprising essentially a non-woven base stratum of uniformly dispersed structural fibers of relatively non-extensible material, and a non-woven surface stratum of uniformly dispersed soluble pore-forming fibers and free of structural fibers to form an initial sheet, said pore-forming fibers being soluble in a solvent which is a non-solvent for the structural fibers, said binder material having a softening temperature below the softening temperature of said fibers; hot-pressing said initial sheet at a temperature above the softening temperature of said binder and below the softening temperature of said fibers, whereby to form a compacted substantially water vapor-impermeable sheet wherein said fibers are embedded in said binder; stretching said compacted sheet 10% to 50% in at least one direction to form channels substantially contiguous with the structural fibers distributed uniformly throughout the base stratum; and dissolving out said pore-forming fibers with a liquid which is a solvent for said pore-forming fibers and a non-solvent for said structural fibers and said binder material, whereby to form a porous, water vapor-permeable sheet of polymeric binder material reinforced with structural fibers and having a porous surface stratum free of fibers.

Preparing Skins for Tanning. Brit. Pat. 751,141. Osterreichische Stickstoffwerke Akt.-Ges. Apl. April 2, 1954.—Unhaired animal skins are prepared for tanning by treatment with thioglycollic acid and/or a water-soluble salt thereof to break down non-skeletal proteins. The compounds may be employed in amounts up to 5% of the weight of the unhaired skins. Alkali metal or ammonium salts or salts of thioglycollic acid with organic bases may be used. The unhaired skins employed have preferably been previously limed, delimed, neutralized and unfleshed.

Manufacture of Leather Sheets Containing Normally Tacky Impregnating Agents. U. S. Pat. 2,769,712. L. H. Wilson, Riverside, Conn., assignor to American Cyanamid Company, New York, N. Y., a corporation of Maine. Apl. Oct. 28, 1952.—1. In a method for making an impregnated leather sheet by the steps of preparing an aqueous stock of leather fibers, adding an aqueous colloidal dispersion of a normally tacky, water-insoluble hydrophobic organic impregnating agent containing a soap as principal dispersing agent therefor, depositing said impregnating agent on the fibers while in aqueous suspension, and forming the fibers into a sheet, the steps of first adding to the fiber suspension at pH between about 3 and 7 a colloidal cationic dimethylolurea water-soluble polyfunctional nitrogen base resin, then adding said aqueous dispersion of tacky impregnating agent containing, in addition, a non-ionic surface-active agent and an anionic surface-active agent selected from the group consisting of the alum-stable sulfonate and the alum-stable sulfate dispersing agents, and sheeting and drying the fibers; the weight of said impregnant being between about 15% and 100% of the weight of the fibers; the weight of said cationic resin being about 5% and 15% of the weight of said impregnant, the weight of non-ionic agent being between 1% and 10% of the weight of the fibers, and the weight of anionic surface-active agent being between 25% and 100% of the weight of non-ionic surface-active agent.

Method of Preparing Phenol Derivatives of Waste Sulphite Liquor, Including Removing the Calcium Ions from the Waste Liquor. U. S. Pat. 2,772,139. H. B. Marshall, Toronto, Ontario, and M. Curran, née Krizsan, Calgary, Alberta, Canada, assignors to Ontario Research Foundation, Toronto, Ontario, Canada. Apl. Feb. 13, 1956.—1. A process for the production of useful substances from calcium base waste sulphite liquor containing calcium lignin sulphonate compounds which consists of removing the calcium ions from the waste sulphite liquor by precipitation with sulphuric acid, heating the decalcified waste sulphite liquor to a temperature of between 100°C. and 150°C. with an excess of a phenol, said phenol being selected from the group consisting of monohydric, dihydric and trihydric phenols and combinations thereof, for a time sufficient to condense the lignin sulphonate compounds with said phenol, and removing the excess phenol.

Tanning Agent Comprising Phenol Derivatives of Waste Sulphite Liquor and Method of Preparing Same. U. S. Pat. 2,772,140. H. B. Marshall and M. Krizsan, Toronto, Ontario, Canada, assignors to Ontario Research Foundation, Toronto, Ontario, Canada. Apl. July 16, 1952.—6. A tanning agent consisting of a combination of natural tannins and a compound derived from waste sulphite liquor by removing the cations from the waste sulphite

liquor by treatment with an ion exchange resin, heating the decationized waste sulphite liquor to a temperature of between 100°C. and 150°C. with an excess of a phenol, said phenol being selected from the group comprising monohydric, dihydric and trihydric phenols and combinations thereof, and removing the excess phenol.

Shoe Sole and Method of Making Same. U. S. Pat. 2,772,196. R. W. Pooley, South Bend, Ind., assignor to United States Rubber Company, New York, N. Y., a corporation of New Jersey. Apl. May 21, 1954.

1. A new article of manufacture comprising a flexible, resilient laminate of a closed-cell, expanded, vulcanized, fused mixture of a thermoplastic vinyl resin, a high-boiling organic liquid plasticizer therefor and a butadiene-acrylonitrile rubbery copolymer, said laminate comprising a plurality of parallel juxtaposed differently colored layers of said mixture integrally bonded together at their interfaces, said layers forming sharp straight lines of demarcation therebetween at exposed surfaces of said laminate transverse to said layers, all of said layers having a compressive resistance of at least 6 pounds per square inch and a density of not over 15 pounds per cubic foot.

CORRECTION

The patent number given in the footnote to Table III, *JALCA*, **51**, 642 (1956) is incorrect. It should be U.S. Patent 2,693,996, instead of 2,643,996.

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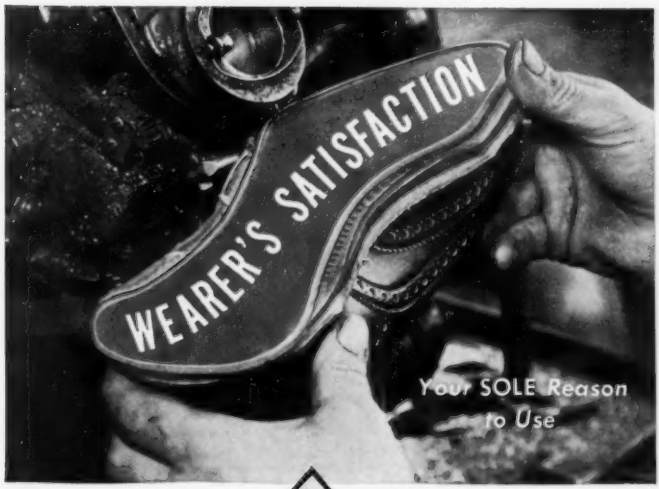

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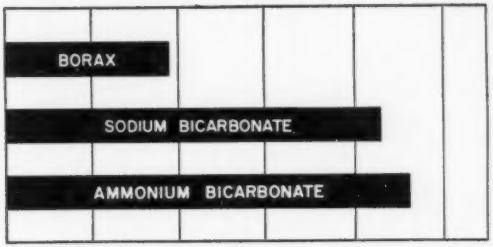
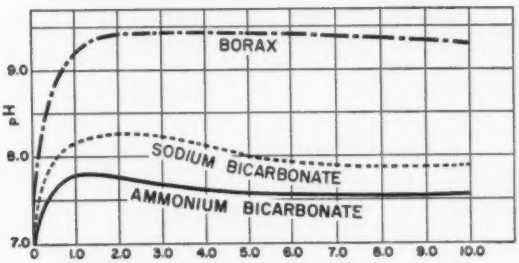


Pounds of hydrochloric acid neutralized by 1 lb. of alkali

at Lower pH for



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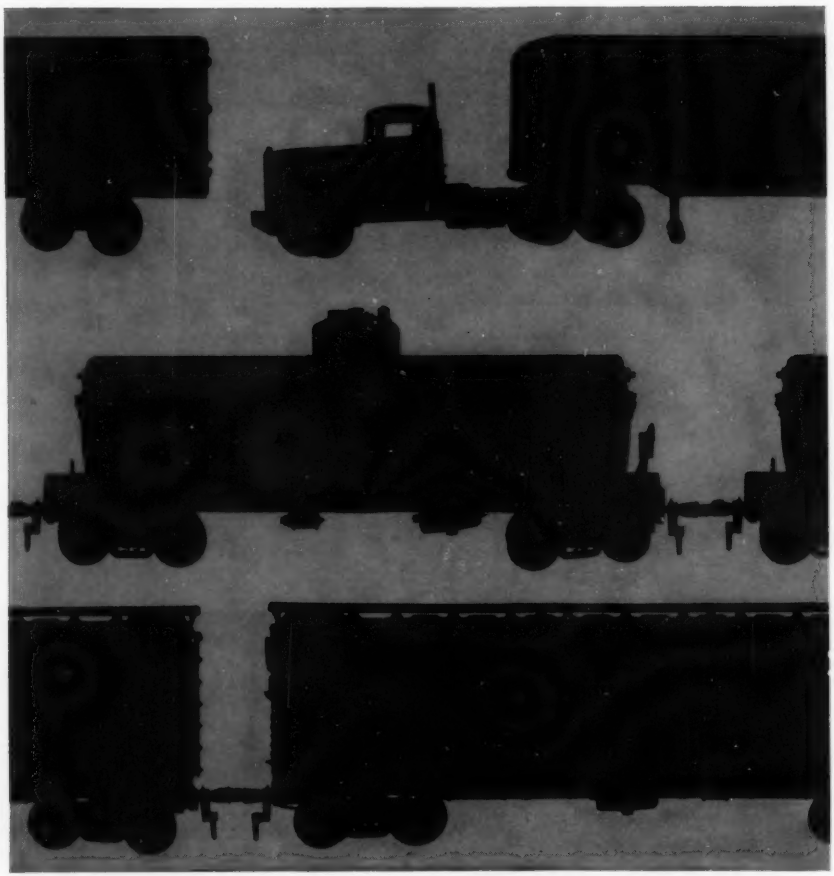

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